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LOW PRESSURE ULTRAFILTRATION SYSTEM FOR WASTEWATER CONTAMINANT REMOVAL

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LOW PRESSURE ULTRAFILTRATION SYSTEM FOR
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FWPCA Research Grant No. WP-01408-01

Progress Report for Period 1 June 1968 - 1 March 1969

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Reported herein is a summary of research progress on Grant No. WP-01408-01, entitled REVERSE OSMOSIS TREATMENT OF WASTEWATERS, from its inception in June 1968 to date. The laboratory apparatus, initially a single cell system, has been redesigned at this point to include three cells in series in a single reservoir recycling arrangement. Although reverse osmosis processes for wastewater treatment contain membranes which selectively pass water, the slight permeability of these membranes to solutes as well has resulted in increasing use of the term ultrafiltration to describe the process. The terms reverse osmosis and ultrafiltration are therefore used interchangeably in this report.

I. OBJECTIVE, SCOPE, AND THEORY

RESEARCH OBJECTIVE

The purpose of ~~this~~ research ~~is~~ to obtain data needed to evaluate and apply reverse osmosis as a process for the treatment of wastewaters. In particular, an improved understanding of the mechanism of separating organic materials from water is essential to development of more suitable membranes and better geometric design of ultrafiltration cells.

The objectives ~~of this study are to~~:

a. Obtain data essential to development of design parameters, including data on liquid diffusion rates, efficiency of separating organic pollutants, and cell operating characteristics for presently-available membranes utilizing waters containing selected organic and inorganic chemicals.

b. Apply ~~the above da~~ta in developing membrane separation techniques for advanced treatment of organic industrial wastes and municipal sewage. In addition to the development of membranes and cells specific to wastewater treatment, this phase of the investigation will consider systems in which reverse osmosis may be utilized in conjunction with chemical additives such as activated carbon and polyelectrolyte coagulant aids. The systems developed will be tested on municipal sewages and industrial wastes.

The reverse osmosis process has been developed to a sophisticated state of technology for desalination of sea water, as shown by the large number of papers published on membranes for separating relatively small sized inorganic ions from water. Since the osmotic pressure of sea water is approximately 350 pounds per square inch (psi), reverse osmosis desalination must be carried out at pressures in excess of this. The first desalination membranes produced only about one gal/ft^2-day of pure water at pressures of 1500 psi, and were therefore far from economically feasible.

Through intensive efforts in membrane research, films of extremely thin cross section and relatively high flux rate have been developed. The salt rejection efficiency has been found to vary with film thickness and porosity, as well as other variables such as temperature, and as a rule those membranes which exhibit the highest flux at lowest operating pressures allow some permeation of salts. Pilot plants now in operation for desalination purposes are designed on the basis of 10 to 20 gal/ft^2 -day flux at operating pressures of 600 to as high as 1500 psi.

Although advances in membrane technology for demineralization of water have encouraged a few field studies on reverse osmosis treatment of contaminated waters, the development of membranes and systems for separation of organic fractions from water must now necessarily be based primarily upon work on inorganic salts, since relatively few studies have been made thus far on pure organic compounds. Organic molecules of larger size than inorganic ions should conceivably be amenable to separation from water by more porous membranes than are used for desalination by reverse osmosis. The use of more porous membranes would allow operation of ultrafiltration systems at more economically feasible pressures than the 600 to 1500 psi now used in the vast majority of reverse osmosis units. With these considerations in mind, a major objective of the studies reported herein is to investigate the removal of organic materials from water at operating pressures of 30 to 50 psi. Of the many major companies producing ultrafiltration equipment, only one has approached membrane treatment in this pressure range, even though new membrane technology gives every indication that low pressure operation is feasible now and surely to be more highly developed in the very near future.

SCOPE

The initial phase of the research has been concerned with the determination of flux rates, removal efficiencies, and other operating characteristics of currently available membranes in order to determine those conditions conducive to most efficient removal of pure organic contaminants in solution. Special attention has been devoted to ultrafiltration membranes which exhibit relatively high flux rates at operating pressures in the range of 50 psi.

The initial studies have consisted of investigating removals of pure organic compounds ranging in size from those with molecular weights in the range of a few hundred (phenolic derivatives and pesticides) to those with molecular weights of several thousand (polysaccharides). Both alkyl and aryl geometric configurations of molecules have been included. The compounds investigated to date have been alkyl benzene sulfonate, lindane, pentachlorophenol, glucose, sucrose, raffinose, and dextrans of varying molecular weights. The range of dextran molecular weights is 10,000 to 110,000.

The data obtained in pure compound studies is being utilized in evaluating presently-known membranes and reverse osmosis processes for their potential in wastewater treatment, and in developing conceptual designs of better membrane processes for reverse osmosis treatment of wastewaters. A basic consideration is the collection and evaluation of data on the basis of the following conditions:

1. Relationship of molecule size and configuration to permeation of organic compounds through reverse osmosis membranes. Some of the organic compounds are in a homologous series. These studies will aid in determining the mechanisms of transport of both water and organics through the membranes.
2. Effect on flux and rejection efficiency of temperature, pressure, and geometry of the membrane cell.
3. Mechanism of flux decrease with time.

THEORY

In the past several years there has been a wealth of articles published on the theoretical aspects of reverse osmosis or ultrafiltration. The initial impetus behind these studies came from desalination studies rather than the use of reverse osmosis systems in water pollution control.

The theoretical work published generally falls into one of three classes:

1) A study of the flow mechanism through the membrane itself.
2) A study of the velocity and concentration profiles for both

laminar and turbulent flow across the membrane, for various system geometries.

3) Attempts to characterize the membrane and molecular parameters of the rejected solute(s) to enable prediction of the operating characteristics and solute rejection of any system.

The above three areas will be discussed below in some detail.

I. Mechanism of Flow Across the Membrane

Because of the wide variety of membrane materials, it is likely that no single theory will describe the behavior of all of them. Since the Loeb-Sourirajan type cellulose acetate membrane is most widely used, much of the theoretical studies conducted to date concern this type of membrane. Michaels, et al(1) have presented a thorough discussion of the flow of water across cellulose acetate membranes and conclude that the flow equation developed by Merten(2) is valid.

$$N_A = K_1(\Delta P - \Delta \Pi)^* \qquad \text{Eq. 1}$$

However, salt (solute) transport is much more complex and three possible transport mechanisms have been postulated:

1) Diffusion of ions within the membrane due to concentration difference.
2) Diffusion of ions in small pores (of approximately the same size as the solute molecule) due to both pressure and

* See end of section for nomenclature.

concentration gradients.

3) Hydrodynamic flow of salt solution through large pores (large relative to the size of the solute molecules).

Recent work by Sherwood(3) and Kimura and Sourirajan (4) suggest that a simpler model may be used.

Sherwood(3) suggests the following equations:

$$N_s = K_2 \Delta P C_{sw} + K_3 (C_{sw} - C_{sp}) \qquad \text{Eq. 2}$$

$$N_A = K_1 (\Delta P - \Delta \Pi) + K_2 \Delta P \Delta C_{Aw} \qquad \text{Eq. 3}$$

Kimura and Sourirajan simplified the above expressions by neglecting pore flow ($K_2 = 0$). Ultimately, if sufficient information is available the brine (solute) side diffusion region and the membrane barrier could be treated as a coupled composite body problem. This has been attempted by Sherwood(3) and Kimura and Sourirajan(5). Another approach is to treat the membrane selectivity in terms of a constant rejection parameter, first defined by Brian(6).

$$R = 1 - \frac{C_{sp}}{C_{sw}} \qquad \text{Eq. 4}$$

This reduces the composite body problem to a single body convective diffusion problem in which R appears as a boundary condition. Using this approach and the simplifications suggested above, a membrane may then be characterized by two parameters: the rejection efficiency, R, and the solvent permeability coefficient of the membrane, K_1.

Johnson and Bennion (7) have taken a slightly different approach to the problem of describing transport through the membrane. They derived(8) a set of equations to describe the flux of binary electrolytes in membranes. Utilizing their equations applied to the transport of sodium chloride and magnesium chloride, they were able to show that the coupling terms were negligible for water flux, but that they are significant for salt flux. This is somewhat in contradiction to the simplifications suggested above.

Johnson and Bennion also presented data on the effect of temperature and composition on the flux rates and coupling terms. Temperatures of 40 to 95°F were studied at concentrations up to 0.1 N.

As a conclusion to this section, the development is given for an equation for the combined solute and water fluxes through a membrane. Neglecting water flux by pore flow:

$$N_A = K_1 (\Delta P - \Delta \Pi) \qquad \text{Eq. 5}$$

Assuming that the osmotic pressure is directly proportional to solute concentration:

$$N_A = K_1 \Delta P \left[1 - \left(\frac{C_{sw} - C_{sp}}{C_{so}} \right) \frac{\Pi_o}{\Delta P} \right] \qquad \text{Eq. 6}$$

The salt flux across the membrane is

$$N_s = (N_A + N_s) C_{sp} \qquad \text{Eq. 7}$$

Combining (6) and (7):

$$(N_A + N_s) = \rho V_w = \frac{K_1 \Delta P}{1 - C_{sp}} \left(1 - \left(\frac{C_{sw}}{C_{so}}\right) \left(1 - \frac{C_{sp}}{C_{sw}}\right) \frac{\pi_o}{\Delta P}\right) \quad \text{Eq. 8}$$

i.e. the combined fluxes may be characterized by K_1 and R. $(1 - \frac{C_{sp}}{C_{sw}})$

II. Solute Side Diffusion Problem

The analytical methods, described below used to attack this problem generally involve the following assumptions:

a) Laminar, isothermal flow (turbulent flow is described briefly later)

b) Incompressible flow

c) Constant viscosity, density, and diffusivity.

d) Constant ΔP

e) Constant permeation velocity. (Vw)

Subject to these assumptions the equations to be solved are:

Continuity equation

$$\nabla \vec{v} = 0 \quad \text{Eq. 9}$$

Equation of Motion

$$\rho\left(\frac{D\vec{V}}{Dt}\right) = -(\nabla \vec{p}) + \mu(\nabla^2 \vec{v}) + (\rho \vec{g}) \quad \text{Eq. 10}$$

Continuity equation for solute

$$\frac{DC_s}{Dt} = D\nabla^2 C_s \quad \text{Eq. 11}$$

plus the general boundary condition at membrane solution interface:

$$V_w C_{sw} - D \left.\frac{\partial C_s}{\partial y}\right|_w = V_w C_{sp} = (1-R)\, V_w C_{sw} \qquad \text{Eq. 12}$$

The problem then becomes the solution of the above equations for a given geometry and flow conditions. In addition, the cases of the so-called entrance region and fully developed flow must be considered. Another possible configuration is transient (batch reverse osmosis) and continuous steady state operation.

Solution of the above equations is difficult; however, the results obtained from approximations are exceedingly useful in the study and prediction of concentration polarization. One of the important features of separation by reverse osmosis is that for nearly all systems the Schmidt number $(\mu/\rho D)$ is very large (about 560 for salt-water systems). This means that the kinematic viscosity is 560 times greater than the diffusion coefficient and that momentum is transferred much more rapidly than mass by molecular transport. Thus, solute concentration will be quite high at the membrane surface in order for the concentration gradient to be sufficiently large for the solute to diffuse back to the bulk stream.

Solutions to the differential equations given above for transient operation have been published by Raridon, Dresner, and Kraus(9), Nakano, Tien and Gill(10), and Williams(11). The reader is referred to these articles for specific details and assumptions made by the authors.

The number of published papers analyzing operation of a continuous laminar flow reverse osmosis system is extensive. Dresner(12) analyzed the case of laminar flow between parallel plates. Using an expression developed by Berman(13) for the axial and transverse velocity profiles, Dresner obtained approximate solutions valid for the inlet and downstream sections of the channel. Sherwood et al(14) also studied the same problem but employed a more accurate form of the velocity equation developed by Berman. Fisher, Sherwood and Brian(15) extended their work to laminar flow in tubes. Results of all of these theoretical studies are summarized and compared by Sherwood(16).

All of the above studies have shown that there is a high degree of polarization in laminar flows. This would suggest that buoyancy effects may be important. To this end Ramandahan and Gill(17) considered the mechanism of free convection in a hyperfiltration system. The momentum and diffusion equations, coupled with the inclusion of a buoyancy term were solved using a perturbation technique.

Theoretical studies have also been published for a non-constant permeation rate. Results of these studies have been presented by Gill, Tien, and Zeh(18), Brian(6), Gill(19), (20), and Srinivasan et al(21), (22).

The theoretical studies of the solute side problem of concentration polarization in laminar flow have shown that concentration polarization is a very significant problem and that methods must be devised to limit it.

All of the preceeding studies have been concerned with laminar flow in reverse osmosis (ultrafiltration) systems. Turbulent flow systems have also received considerable attention in the past few years.

In laminar flow the important transport mechanisms are axial convection, radial (or transverse) convection and radial molecular diffusion. In turbulent flow transport of mass by radial eddy diffusion is important in determining concentration profiles.

Sherwood(14, 16), and Brian(23) have employed the Nernst film theory and Deissler(24) eddy diffusion models for turbulent transport to describe concentration polarization in reverse osmosis systems. These models assume that all the resistance to mass transfer is concentrated in a very thin region next to the interface. The film theory also assumes this thin layer to be laminar. From these assumptions and employing the Chilton Colburn j_D factor analogy the required mass transfer coefficient may be calculated. Also the solute concentration at the membrane surface may be estimated.

Theoretical calculation of the velocity and concentration profiles for turbulent flow is not as well advanced as for laminar flow. In particular the analyses break-down for relatively large distances from the inlet where the fraction of feed removed is sufficient to alter the eddy diffusivity. However, the theory does show that for systems having the same inlet and wall Reynolds numbers concentration polarization increases with increasing values of the Schmidt number. In general use of the either the film theory or eddy diffusivity models will give comparable answers.

III. Prediction of Solute Rejection from Molecular Parameters

To date relatively little research has been published on attempts to predict solute rejection from a knowledge of such parameters as membrane pore size, molecular diameter, molecular configuration, etc. One of the more extensive series of experimental studies in this regard was conducted by Blunk(24). He investigated solute rejection for a fairly wide range of types and sizes of organic molecules. From an analysis of the data Blunk concluded that the relative ratio of pore diameter and molecular diameter cannot solely be used to correlate solute rejection.

Merten et al(25) very recently published results of their and other studies on organic removal by reverse osmosis, including tertiary treatment of sewage effluent, fruit juices, pulping wastes and sugars.

Most of the studies which they discuss are for cellulose acetate systems. These membranes serve as an excellent barrier to colloids, other suspended matter and dissolved organics. Significant permeation rates were observed for some (not all) small organics. Those with high permeation rates were usually oxygenated organics. There would appear to be a large amount of theoretical and experimental work still to be done in the area of predicting solute rejection from readily measurable membrane and molecular parameters.

Nomenclature

C_{Aw} = mass fraction of solvent on solute side of membrane

C_s = mass fraction of solute

C_{sw} = mass fraction of solute on solute side of membrane

C_{sp} = mass fraction of solute in product stream

D = molecular diffusion coefficient

$\vec{g}$ = gravitational acceleration vector

K_1 = solvent permeability coefficient of membrane defined by Eq. 1

K_2 = pore flow coefficient of membrane defined by Eq. 2 and Eq. 3

K_3 = solute permeability coefficient of membrane defined by Eq. 2

N_A = solvent flux

N_s = solute flux

ΔP = applied pressure drop across membrane

R = membrane rejection factor defined by Eq. 1

t = time

$\vec{V}$ = velocity vector

V_w = permeation velocity of solute through the membrane

y = transverse or radial coordinate

Greek Letters:

μ = absolute viscosity of solution

Π_o = osmotic pressure corresponding to concentration C_s

$\Delta\Pi$ = difference in osmotic pressure on either side of the membrane

ρ = density of solution

Operators:

∇ = generalized "del" operator

∇^2 = generalized Laplacian

D = substantial derivative

∂ = partial derivative

II. EXPERIMENTAL APPARATUS, METHODS, AND MATERIALS

MULTI-CELL SYSTEM

Preliminary studies using a single ultrafiltration cell as the filtration mechanism in a laboratory constructed recycling system, demonstrated that the cell was well-suited for research type investigations. This cell, developed by the Dorr-Oliver Company of Stamford, Connecticut, was constructed of acrylic plastic and possessed sufficient structural strength for withstanding operating pressures up to 100 psi (maximum range utilized in low pressure ultrafiltration research). Based upon the success of these studies, a similar but multi-cell laboratory unit was utilized for the research described in this section of the report.

The schematic diagram shown in Fig. 1 represents a flow sheet of that multi-cell ultrafiltration system. The basic unit, purchased from the Dorr-Oliver Company, was modified for operational convenience and is described in detail below.

COMPONENTS OF THE ULTRAFILTRATION SYSTEM

The three gallon capacity reservoir, as depicted in the schematic diagram and shown in the photograph of Fig. 2, was constructed of stainless steel to accommodate a maximum working pressure of 100 psi. The reservoir may be pressurized from an external tank of nitrogen gas visible on the left. Modifications to the factory supplied reservoir included a sampling tap (simple gate valve), temperature probe (thermistor), and cooling coil. The cooling coil circulates water from an external constant temperature source and maintains a 20 ± 0.5°C reservoir temperature.

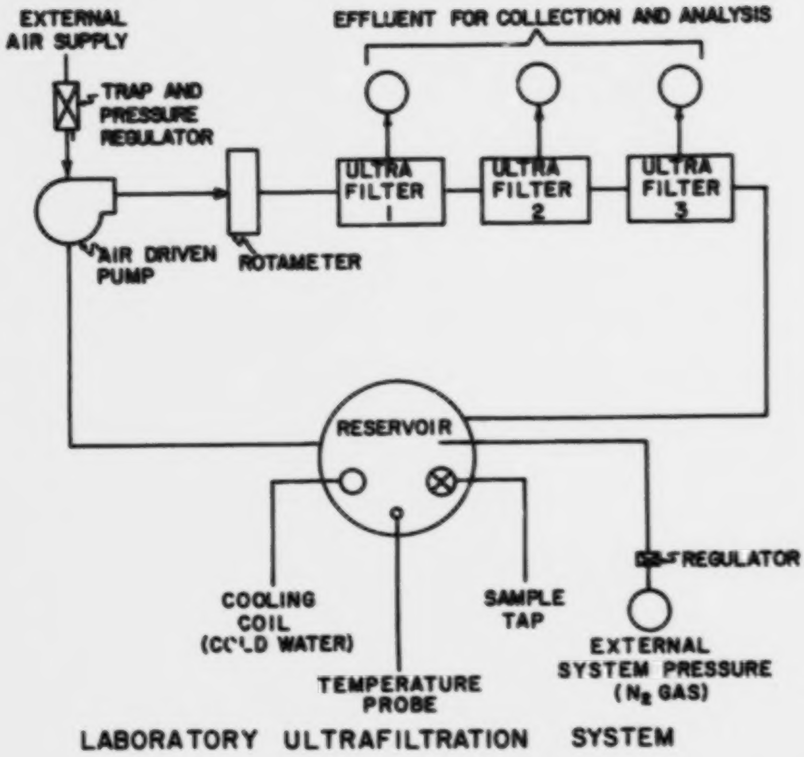
EXTERNAL AIR SUPPLY
TRAP AND PRESSURE REGULATOR
AIR DRIVEN PUMP
ROTAMETER
EFFLUENT FOR COLLECTION AND ANALYSIS
ULTRA FILTER 1
ULTRA FILTER 2
ULTRA FILTER 3
RESERVOIR
REGULATOR
COOLING COIL (COLD WATER)
TEMPERATURE PROBE
SAMPLE TAP
EXTERNAL SYSTEM PRESSURE (N_2 GAS)
LABORATORY ULTRAFILTRATION SYSTEM

Figure 1. FLOW DIAGRAM OF THE MULTI-CELL LABORATORY ULTRAFILTRATION UNIT.
System filtration pressure is provided by external pressurized nitrogen gas. The pump is powered by a standard laboratory air supply which is trapped and regulated prior to use as the driving force.

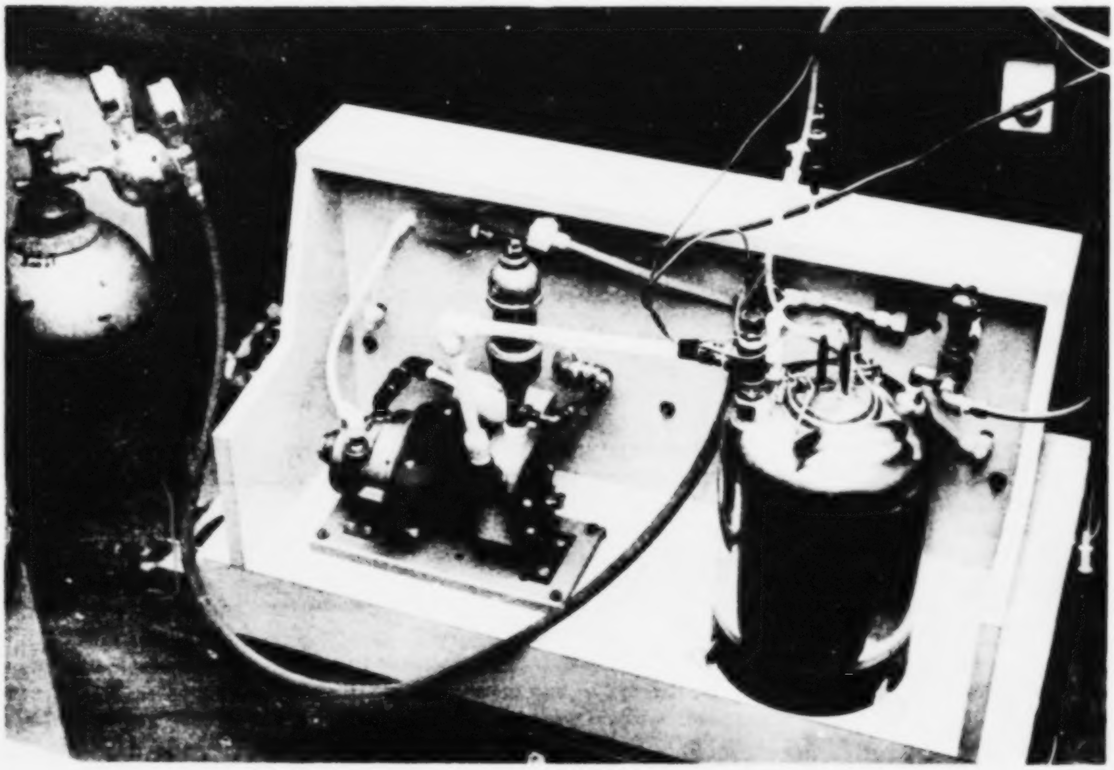

Figure 2. REAR VIEW OF THE LABORATORY ULTRAFILTRATION UNIT. The reservoir has been modified to include a sample tap (right), cooling coil (internal, center), and temperature probe (left). A blowoff valve is visible to the left of and behind the sample tap. The air driven pump is fitted with an air cushion damper to equalize flow variations.

The sample to be filtered is circulated from the reservoir by means of the pump shown on the left in Fig. 2. The pump itself is unique in that it is air driven, thereby lowering inherent additions of heat to the system. The pumping capacity of 2.5 gallons per minute (gpm) was controlled ±0.1 gpm by means of a rotameter on the front side of the unit. The only modification to the pump was the addition of an air cushion damping reservoir (visible in Fig. 2) to eliminate the amplitude of flow pulsation. Air was supplied to the pump from a 100 psi laboratory air line. A filter trap and pressure reducing valve preceeding the pump insured a clean, dry, constant pressure drive for operation.

The photograph in Fig. 3 shows a clear view of the front of the ultrafiltration unit. The rotameter at right center indicates the pumping rate which is varied by means of the pump speed controller. Although the system pressure was controllable directly from the nitrogen cylinder's two-stage pressure regulator, the unit was factory equipped with an auxilliary gage and control valve visible in the upper left.

The ultrafiltration cells were arranged in series and fitted with brass stopcocks at the permeate effluent ports. The permeate was forced through the ports (fitted with flexible tubing) and collected in the graduate cylinders visible in the lower right corner of Fig. 3.

An exploded view of an ultrafiltration cell is depicted in Fig. 4. In actual use, as shown in Fig. 3, the units were inverted. After insertion of the membrane between the porous spacer and "O" rings, the upper and lower portions of each cell were clamped together by means of the bolts and wing-nuts visible in Fig. 3.

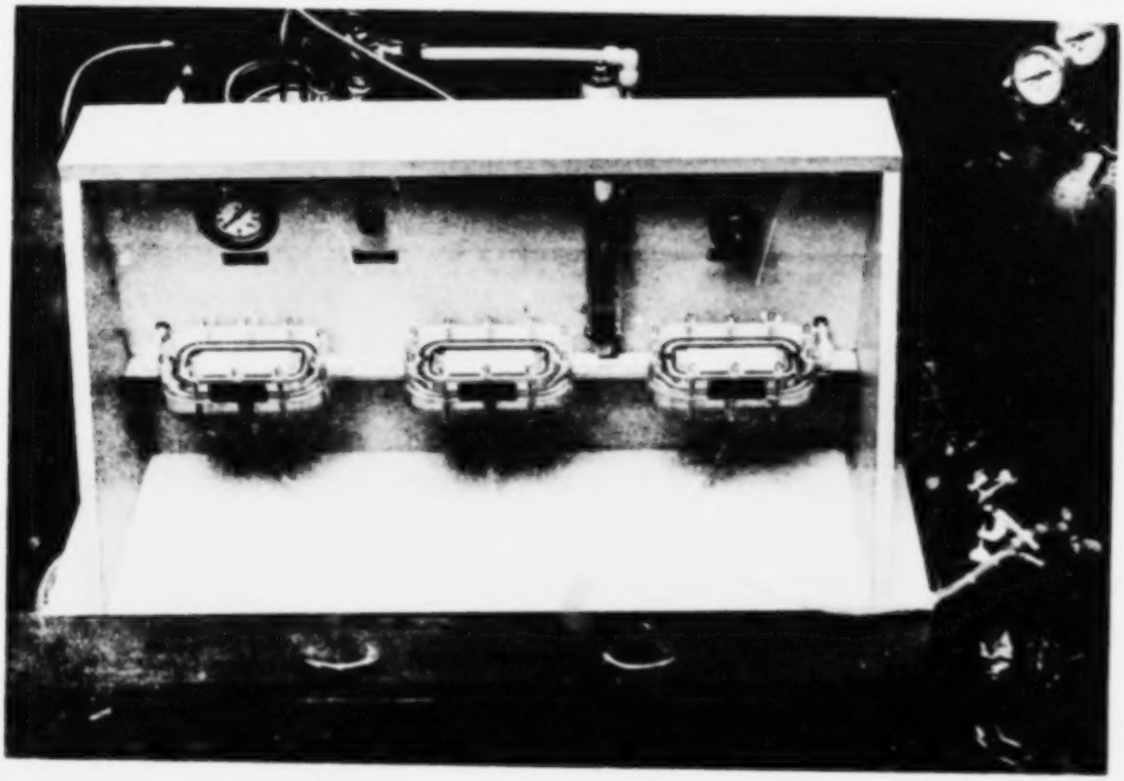

Figure 3. FRONT VIEW OF THE LABORATORY ULTRAFILTRATION UNIT. The system pressure gage and controller are visible at the upper left. Flow rates are regulated by the pump speed controller (upper right) and reflected by the rotameter. The compressed gas cylinder maintains a constant filtration pressure. Permeate from each cell is collected in the graduated cylinders (lower right). Stopcocks at the permeate drainage ports are barely visible beneath each cell.

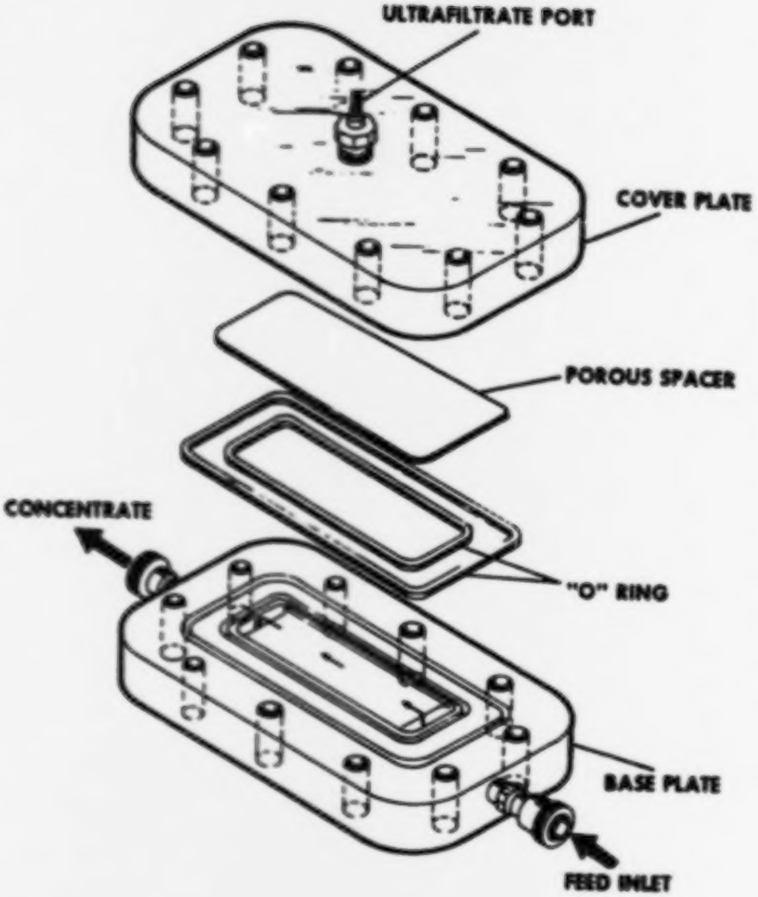
ULTRAFILTRATE PORT
COVER PLATE
POROUS SPACER
CONCENTRATE
"O" RING
BASE PLATE
FEED INLET

Figure 4. ASSEMBLY VIEW OF ULTRAFILTRATION CELL. Membranes are sandwiched between the "O" rings and porous spacer prior to bolting the cell halves together. In operation (as in Fig. 3) the cells are inverted.

Since each cell was of standard area (i.e.--the area surrounded by the inner "O" ring), flux rates were easily computed by measuring the rate of permeate flow through each cell. The addition of stopcocks to each drainage port permitted the use of any, all, or none of the cells as needs dictated.

EXPERIMENTAL METHODOLOGY

The following methodology was developed for determining the overall efficiency of the ultrafiltration system in removing contaminants from an incompressible fluid media. It is of maximum import to note that the unit employed was operated with a pump drive pressure of 50 psi and a system filtration pressure of 40 psi. At these relatively low operating pressures, standard compression fittings could be employed on all tubing, and all system joints were leak-proof when sealed with ordinary "Teflon" pipe tape.

Sample preparations: For the initial series of laboratory tests, pure chemicals were mixed with distilled water and filtered through the unit. Initial substrate concentrations were set at 500 mg/l, with quantities based on reservoir volume of 11 liters. Substrate detection in both the reservoir and permeate was based on the Chemical Oxygen Demand (COD) test as outlined in Standard Methods(26). In order to relate substrate concentration to COD, a series of dilutions was prepared for every chemical and analyzed for COD. A calibration curve relating COD to unremoved substrate concentration was then prepared for each chemical.

Operational procedure: Initially, the stopcocks at all three permeate drainage ports were closed and the reservoir filled with prepared test sample. The pump was then started and the flowrate adjusted to a predetermined level. Air initially present was bled from the system by means of a blowoff valve visible on the reservoir in Fig. 2. Nitrogen gas was then introduced into the reservoir and the pressure adjusted by means of the regulators visible in Fig. 3. Before opening the permeate drainage ports, a reservoir sample was drawn from the tap shown in Fig. 2. This sample served as a check on the initial substrate concentration. The ultrafiltration system was in equilibrium (i.e., equal pressure on both sides of the membrane) at this point.

To initiate the ultrafiltration process, the stopcocks on the permeate drainage ports were then opened. This resulted in a pressure drop across the membranes, from full system pressure on the upper face to atmospheric pressure on the permeate drainage side. Cumulative permeate measurements were taken hourly for each cell.

After four hours of operation, a 50 ml sample was taken from each drainage tube, as well as the reservoir tap. Each sample was analyzed for COD and the results converted to mg/l substrate present. The reservoir sample served as a convenient check, in that any reducation in substrate concentration of the permeate should be reflected by an increased substrate concentration in the reservoir.

Each laboratory "run" extended over an 8 hour period with the above sampling technique repeated at the close of each test.

MEMBRANE MATERIALS AND SUBSTRATES

The membranes employed for testing with the multi-cell ultrafiltration unit were supplied by the Dorr-Oliver Company. In view of the fact that membrane technology is currently in its embryonic stages, the following proprietary description of the membranes was authorized by a representative of the supplier:

> "The ultrafiltration membranes used in these systems are non-cellulosic organic polymers. The membranes are a asymmetric; that is, they are comprised of an extremely thin surface layer (or skin) and a porous substructure of the same material. The porous substructure is required solely for mechanical strength. The skin is approximately five microns in thickness; whereas, the total membrane thickness is six to 8 mils. Since pressures of 20 to 50 pounds per square inch are usually used in these systems, the membranes are reinforced with a non-woven material to give added support."

In addition, each membrane was supported by a phenoxy spacer (Fig. 4) to insure a tight seal within the cell.

All three ultrafiltration cells were fitted with identical membranes for each substrate series filtered. Upon completion of investigations on a series of substrates through one type of membrane, a new type membrane was installed and tested with the same compounds. Two types of membranes investigated to date were factory designated as AP-006 and BP-009 respectively.

The following series of substrates were filtered through the system fitted with membrane AP-006 and then with membrane BP-009.

Substrate	Formula weight (approx)
Glucose	180
Sucrose	342
Raffinose	595
*Dextran T-10	10,000
*Dextran T-20	20,000
*Dextran T-40	40,000
*Dextran T-70	70,000
*Dextran T-110	110,000

*Products of the Pharmacia Company, Uppsala, Sweden

This series was chosen to determine the effect of increased molecular weights on substrate removal via the mechanism of ultrafiltration.

III. EXPERIMENTAL RESULTS AND DISCUSSION

MULTI-CELL UNIT

Studies utilizing sugars and higher molecular weight carbohydrate organic compounds for the initial multi-cell ultrafiltration investigations are in progress at the present time. Results reported here are, therefore, of a preliminary nature. A considerable quantity of raw data has been collected, which is included below. Analyses in depth must depend upon completion of the pure compound organic studies, and at this point the research program is proceeding according to the schedule set forth originally.

AP-006 MEMBRANE

Each of the three cells in the multi-cell unit was fitted with identical AP-006 membranes. Permeate from each cell was collected and analyzed separately, constituting three replicate sets of data for each investigation.

As described in Chapter II, the three cells were connected in series, with the bulk fluid being recycled back to a single reservoir. In filtering the Dextran series of organics at high solute rejection efficiencies, concentrations of solute in the system increased with time owing to the buildup of rejected solute remaining within the recycling system. This resulted in an opportunity to correlate solute rejection with concentration for each of these compounds.

The experimental data collected utilizing the AP-006 membrane is presented in Table 1. The data has been programmed for computer analysis, with the initial UMASS FAST FORTRAN program shown in the

TABLE 1

REMOVAL OF SOLUTES USING AP-006 MEMBRANE AT 40 PSI, 1.0 GPM, AND 20.0°C

Substrate	Time (Hr)	Substrate Concentration (mg/1)				Per Cent Removal			
		Reser-voir	Left Cell	Middle Cell	Right Cell	Left Cell	Middle Cell	Right Cell	Average
Glucose	4	457.1	453.1	449.2	457.1	1.0	2.0	0	1.0
	8	524.0	512.2	535.9	531.9	2.0	-2.0	-2.0	-0.7
Sucrose	4	393.9	488.7	503.3	496.0	-24.0	-28.0	-26.0	-26.0
	8	488.7	466.8	488.7	503.3	-4.0	0	-3.0	-2.3
Raffinose	2	498.8	505.1	515.6	498.8	-1.0	-3.0	0	-1.3
	4	528.1	482.0	492.5	498.8	9.0	7.0	6.0	7.3
	6	532.3	513.5	513.5	500.9	4.0	4.0	6.0	4.7
	8	540.7	500.9	505.1	484.1	7.0	7.0	10.0	8.0
Dextran 10	2	536.8	333.7	332.0	330.2	38.0	38.0	38.0	38.0
	4	550.9	328.5	370.8	374.0	40.0	33.0	32.0	35.0
	6	543.9	326.7	324.9	346.1	40.0	40.0	36.0	38.7
	8	603.9	367.3	362.0	353.2	39.0	40.0	42.0	40.3

TABLE 1 (continued)

Substrate	Time (Hr)	Substrate Concentration (mg/1)				Per Cent Removal			
		Reser-voir	Left Cell	Middle Cell	Right Cell	Left Cell	Middle Cell	Right Cell	Average
Dextran 20	2	494.8	309.7	300.5	306.0	37.0	39.0	38.0	38.0
	4	568.1	295.0	320.7	287.7	48.0	44.0	49.0	47.0
	6	601.1	309.7	317.0	315.2	48.0	47.0	48.0	47.7
	8	689.1	350.0	344.5	353.7	49.0	50.0	49.0	49.3
Dextran T40	4	492.3	238.9	246.1	221.0	51.0	50.0	55.0	52.0
	8	697.1	233.6	240.7	230.0	66.0	65.0	67.0	66.0
Dextran T70	4	561.9	232.6	236.2	218.3	59.0	58.0	61.0	59.3
	8	701.5	75.2	64.4	57.3	89.0	91.0	92.0	90.7
Dextran T110	4	523.7	340.7	362.3	351.5	35.0	31.0	33.0	33.0
	8	566.7	358.7	376.6	412.5	37.0	34.0	27.0	32.7

Appendix. Modifications of this program and the development of additional sub-routines will allow analysis of the laboratory data and correlation with theoretical concepts of reverse osmosis and ultrafiltration. Selected portions of the remote console "Teletype" printout are shown in Table 1.

It can be seen that the AP-006 membrane was ineffective in rejecting small sugar molecules, such as glucose and sucrose, with separation efficiency on the order of 6 to 10 per cent beginning with the filtration of raffinose. It is to be noted that the molecular weights of these compounds increase from 180 to 342 to 595 respectively, indicating that in this series poor rejection occurs at molecular weights below the range of 500 to 1000.

The lowest molecular weight Dextran was rejected with considerably greater efficiency than was raffinose. The difference in molecule size between compounds of molecular weight 595 and those of molecular weight 10,000 is however, extremely great. Compounds with molecular weights between these values remain to be investigated in order to explore further the relationships between solute rejection and molecular size and configuration.

The Dextran series of compounds with molecular weights from 10,000 to 70,000 were removed by the AP-006 membrane with increasing efficiency in direct proportion to their molecular weight. There was, in addition, increasing rejection efficiency with duration of filtration. This would suggest that a film of solute was building up on the surface of the membrane during the ultrafiltration experiment, or that molecules of solute became entrapped in the intertices of the membrane as filtration proceeded, thereby increasing the "tightness" of the membrane with time. It was interesting to note that permeate flux rates did not significantly change throughout eight hour ultrafiltration periods of each particular study. On the other hand, the average flux rate over the eight hour test period tended to decrease with increasing size of solute molecules. On the AP-006 membrane this flux rate varied from 35 gals/ft^2/day with Glucose to 20 gals/ft^2/day with Dextran 110.

Dextran 110, with a molecular weight of 110,000 was rejected with less over-all efficiency than the Dextran 70. The initial removal efficiency for the two compounds was similar, but in the Dextran 110 experiments the removal efficiencies did not increase with time.

BP-009 MEMBRANE

The series of studies utilizing the BP-009 membrane was carried out in a manner identical with those on the AP-006 membrane. The results of these studies are shown in Table 2. It can be seen that solute rejection utilizing this membrane was somewhat similar to that of the AP-006 membrane but some differences, based upon initial investigation, can be noted. Although the sugar compounds, glucose, sucrose, and raffinose, were poorly rejected with approximately the same efficiency as with the AP-006 membrane, the major difference between the two membranes can be noted in the Dextran series. The lower molecular weight Dextrans were rejected in the 60 to 70 per cent efficiency range, while on the AP-006 membrane the lower weight Dextrans were rejected only in the 35 to 50 per cent range. Rejection of the large Dextran molecules was generally more pronounced throughout the BP-009 studies. It is interesting to note that the per cent

TABLE 2

REMOVAL OF SOLUTES USING BP-009 MEMBRANE AT 40 PSI, 1.0 GPM, AND 20.0°C

Substrate	Time (Hr)	Substrate Concentration (mg/l)				Per Cent Removal			
		Reservoir	Left Cell	Middle Cell	Right Cell	Left Cell	Middle Cell	Right Cell	Average
Glucose	3	496.1	456.7	464.6	456.7	8.0	6.0	8.0	7.3
	8	472.[illegible]	480.3	480.3	464.6	-2.0	-2.0	2.0	-0.7
Sucrose	3	495.4	491.6	480.5	521.4	1.0	3.0	-5.0	-0.3
	8	499.1	514.0	461.8	484.2	-3.0	7.0	3.0	2.3
Raffinose	3	567.1	545.8	537.3	597.0	4.0	5.0	-5.0	1.3
	8	520.2	503.2	511.7	494.7	3.0	2.0	5.0	3.3
Dextran 10	3	514.4	253.7	185.8	250.1	51.0	64.0	51.0	55.3
	8	893.1	289.4	242.9	300.1	68.0	73.0	66.0	69.0

TABLE 2 (continued)

Substrate	Time (hr)	Substrate Concentration (mg/1)				Per Cent Removal			
		Reser-voir	Left Cell	Middle Cell	Right Cell	Left Cell	Middle Cell	Right Cell	Average
Dextran 20	3	515.1	155.6	100.1	148.2	70.0	81.0	71.0	74.0
	8	756.0	177.9	122.3	185.3	76.0	84.0	75.0	78.3
Dextran T40	3	561.1	84.3	73.3	91.7	85.0	87.0	84.0	85.3
	8	718.7	84.3	73.3	104.5	88.0	90.0	85.0	87.7
Dextran T70	3	547.0	16.4	12.8	27.3	97.0	98.0	95.0	96.7
	8	743.9	87.5	69.3	--	88.0	91.0	--	89.5
Dextran T110	3	618.3	201.9	118.2	50.9	67.0	81.0	92.0	80.0
	8	723.8	200.0	170.9	76.7	72.0	76.0	89.0	79.0

rejection did not increase substantially throughout the course of the 8 hour experiment with the BP-009 membrane as was the case with the AP-006 membrane. In fact, in two of the experiments, there was a slight decrease in rejection efficiency near the end of the run as compared with that obtained at the end of three hours. The BP-009 membrane was in general a more "tight" membrane, with flux rate varying from 25 gals/ft^2/day on glucose to 10 gals/ft^2/day on Dextran 110. It was observed in the case of the BP-009 membrane that although efficiency of rejection was low with glucose and other small molecules, increased molecule size resulted in greater solute removal than was observed utilizing AP-006 membranes.

DISCUSSION AND RESULTS

The multi-cell ultrafiltration studies indicate, on the basis of the preliminary data, that the separation of organic matter from water by membranes at low operating pressures is feasible when utilizing "loose" membranes. The particular membranes under investigation at the present time allow a water flux rate of as high as 35 gals/ft^2/day at 40 psi which is within an economic range of production of potable water from a contaminated source. Although these studies show that the two porous membranes investigated are not suitable for separating small organic ions and molecules from aqueous solution, such separation was not anticipated because of the characteristics of the membrane.

It must be emphasized that the studies on porous membranes are only now well-initiated and research productivity will be increasing in magnitude as the studies progress. Basic questions such as determination of concentration polarization characteristics and the nature of membrane fouling will be solved through the development of much more data than is presently available from the few months in which the multi-cell laboratory unit has been operating.

Progress to date on multi-cell studies can be summarized by stating that the laboratory unit has been installed and has been operating successfully for several series of runs on pure organic compounds. Redesign of the unit in order to make minor improvements has been carried out since initiation of the studies, and the results have indicated to date that other modifications will be made in the near future. These will consist primarily of returning the permeate to the makeup reservoir so that the bulk fluid will contain a consistent concentration of solute throughout each study. Data collection has been organized, and a computer program for analysis of data has been developed and implemented.

IV. SINGLE CELL EXPERIMENTAL RESULTS

The initial ultrafiltration studies, upon which investigations described in the preceeding chapters were based, were initiated on a single ultrafiltration system construction in the laboratory. The cell utilized in this system, shown in Fig. 5, was found to be satisfactory for continued studies without modification. Three such cells were then utilized in the milti-cell system.

The results of the single cell studies are included as an appendix to the report. A relatively "tight" cellulose acetate membrane was utilized for these studies. This membrane rejected small molecule organic solutes, with molecular weights in the order of several hundred. Three compounds, lindane, alkylbenzene sulfonate, pentachlorophenol were investigated. The cellulose acetate membrane was particularly effective in rejecting ABS molecules and less effective in removing lindane and pentachlorophenol.

The single cell studies, like the multi-cell studies to date, have been preliminary in nature and have resulted in development of equipment, laboratory procedures, and initial data sufficient to provide the basis for the concerted research effort now in progress.

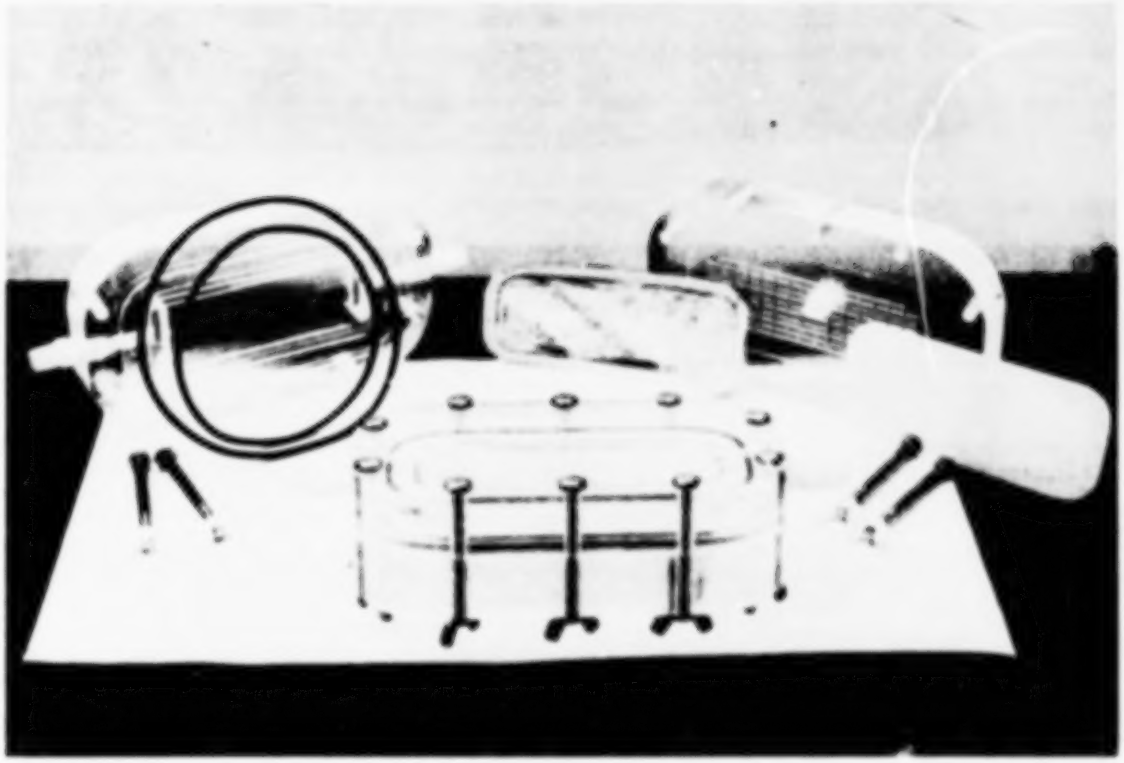

Figure 5. RESEARCH ULTRAFILTRATION CELL.
Shown are a complete cell in the foreground and its component parts in the background. The component parts consist primarily of the membrane, its porous backing, and the lucite cell body. In this photograph the membrane has been used for a series of studies, and therefore it is coated with a deposit of contaminants which have been removed from the water.

V. FUTURE WORK

The ultrafiltration research studies are expected to increase substantially in volume over the next year. Over the past year three Ph.D. candidates and two M.S. candidates have been associated with the study, and the production to date has been one M.S. thesis. The Ph.D. candidates will begin devoting full time to the ultrafiltration studies upon completion of their doctoral coursework and examinations this year. In addition, two additional Ph.D. candidates will begin their research studies in ultrafiltration of organic contaminants at low pressures during the coming year. One of these, a chemist, has been and will continue to be funded throughout her Ph.D. program by means of an FWPCA Research Training Grant, and the other has been supervising reverse osmosis studies at the Ft. Belvoir Army Research and Development Research Laboratories prior to enrolling for his Ph.D. program in September 1968. It is anticipated that his ultrafiltration studies will be supported by sources other than the FWPCA 01408 Grant. It is anticipated that the five Ph.D. candidates plus several Master candidates continuing research over the next two years will provide an extensive amount of research information on ultrafiltration, concentration polarization problems, development of better membranes and systems, and other facets pertaining to ultrafiltration of organic contaminants at low pressures.

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APPENDIX

UMASS FAST FORTRAN PROGRAM FOR ULTRAFILTRATION DATA ANALYSIS

```
010 PROGRAM REVOS
015 PRINT 20
021 INPUT,INS
022 NYES-3HYES
023 NO=2HNO
024 IF( INS.EQ.NYES )26,25
025 IF( INS.EQ.NO ) 51,20
026 PRINT 27
027 FORMAT(*ENTER DATA AS FOLLOWS*)
028 PRINT 29
029 FORMAT(*N,F,ST,DLRES,DLCEL,MW,IT*)
030 PRINT 31
031 FORMAT(*WHERE*)
032 PRINT33
033 FORMAT(*N=THE NUMBER OF SAMPLING PERIODS PER RUN*)
034 PRINT 35
035 FORMAT(*F=THE FACTOR FOR CONVERTING COD TO MG/LITER*)
036 PRINT 37
037 FORMAT(*ST=THE NUMBER OF ML. NEEDED TO STANDARDIZE TITRANT*)
038 PRINT 39
039 FORMAT(*DLRES AND DLCEL=THE DILUTION RATIOS FOR THE RESERVOIR
040A AND THE CELLS*)
041 PRINT 42
042 FORMAT(*MW=THE MOLECULAR WEIGHT OF THE SOLUTE*)
043 PRINT 44
044 FORMAT(*IT=THE TIME INTERVAL BETWEEN SAMPLES*)
045 PRINT 46
046 FORMAT(*THEN ENTER THE FOLLOWING FOR EACH TIME INTERVAL*)
047 PRINT 48
048 FORMAT(*RES,LC,MC,RC:.WHERE THESE ARE THE DIFFERENCES IN ML.TITRANT
049A BETWEEN*)
050 PRINT 51
051 FORMAT(*THE BLANK AND THE SAMPLES FROM EACH CELL AND THE RESERVOIR*)
```

```
052 DIMENSION COD(30,4),CONC(30,4), SEPAR(30,3), PCNT(30,3)
053 II=1
054 READ,NUMB
055 READ, TEMP,PRES,FLOW
060 READ,N,F,ST,DLRES,DLCEL,MW,IT
062 ITM=0
065 CODF=2.5*400.0/ST
070 DO 507 I=1,N
075 READ,RES,XLC,XMC,RC
080 COD(I,1)=CODF*DLRES*RES
085 COD(1,2)=CODF*DLCEL*XLC
090 COD*I,3)=CODF*DLCEL*XMC
095 COD(I,4)=CODF*DLCEL*RC
100 CONC(I,1)=F*COD(I,1)
105 CONC(I,2)=F*COD(I,2)
110 CONC(I,3)=F*COD(I,3)
115 CONC(I,4)=F*COD(I,4)
135 SEPAR(I,1)=CONC(I,1)/CONC(I,2)
140 SEPAR(I,2)=CONC(I,1)/CONC(I,3)
145 SEPAR(I,3)=CONC(I,1)/CONC(I,4)
150 PCNT(I,1)=(CONC(I,1)-CONC(I,2))/CONC(I,1)
155 PCNT(I,2)=(CONC(I,1)-CONC(I,3))/CONC(I,1)
160 PCNT(I,3)=(CONC(I,1)-CONC(I,4))/CONC(I,1)
165 IF(I.GT.1)500,170
170 IF(MW.EQ.198)215,175
175 IF(MW.EQ.342)230,180
180 IF(MW.EQ.595)245,185
185 IF(MW.EQ.10000)260,190
190 IF(MW.EQ.20000)275,200
200 IF(MW.EQ.40000)290,205
205 IF(MW.EQ.70000)305,210
210 IF(MW.EQ.110000)320,215
215 PRINT220
220 FORMAT(*RESULTS OF GLUCOSE RUN*//)
```

```
225 GO TO 400
230 PRINT 235
235 FORMAT(*RESULTS OF SUCROSE RUN*//)
240 GO TO 400
245 PRINT 250
250 FORMAT(*RESULTS OF RAFFINOSE RUN*//)
255 GO TO 400
260 PRINT 265
265 FORMAT(*RESULTS OF DEXTRAN 10 RUN*//)
270 GO TO 400
275 PRINT 280
280 FORMAT(*RESULTS OF DEXTRAN 20 RUN*//)
285 GO TO 400
290 PRINT 295
295 FORMAT(*RESULTS OF DEXTRAN 40 RUN*//)
300 GO TO 400
305 PRINT 310
310 FORMAT(*RESULTS OF DEXTRAN 70 RUN*//)
315 GO TO 400
320 PRINT325
325 FORMAT(*RESULTS OF DEXTRAN 110 RUN*//)
400 PRINT 405
405 FORMAT(*NO OF     COD TO     ML. TO           DILUTION*)
410 PRINT 415
415 FORMAT(*SAMPLES   CONC       STANDARDIZE      FACTORS*)
420 PRINT 425
425 FORMAT(*PER RUN   FACTOR     TITRANT          RES      CELL*)
430 PRINT 435,N,F,ST,DLRES,DLCEL
435 FORMAT(15,F11.3,F15.3,F10.1,F9.1//)
440 PRINT 445
445 FORMAT(*MOLECULAR                 REVERSE OSMOSIS SYSTEM*)
450 PRINT 455
455 FORMAT(*WEIGHT          TEMP.       FLOW(GPM)      PRES(PSI)*)
460 PRINT 465,MW,TEMP,FLOW,PRES
```

```
465 FORMAT(19,F12.1,F10.1,F15.1//)
470 PRINT 475
475 FORMAT(5X,*CHEMICAL  OXYGEN  DEMAND     SOLUTE    CONCENTRATION*)
480 PRINT 485
485 FORMAT(5X,*RESER  LEFT  MIDDLE   RIGHT  RESER  LEFT   MIDDLE   RIGHT*)
490 PRINT 495
495 FORMAT(*TM  VOIR   CELL   CELL    CELL  VOIR   CELL   CELL    CELL*)
500 PRINT 505,ITM,(COD(I,J),J=1,4),(CONC(I,J),J=1,4)
505 FORMAT(13,F8.1,F6.1,F6.1,F8.1,F8.1,F6.1,F6.1,F8.1)
506 ITM=ITM+IT
507 CONTINUE
508 PRINT 509
509 FORMAT(5X,*-----------------------------------------------------*/)
510 PRINT 515
515 FORMAT(5X,*RESERVOIR CONC/CEL CONC                  PCNT REMOVAL*)
520 PRINT525
525 FORMAT(5X,*LEFT     MIDDLE    RIGHT        LEFT       MIDDLE    RIGHT*)
530 PRINT 535
535 FORMAT(*TM  CELL     CELL      CELL         CELL        CELL       CELL*)
536 ITM=0
537 DO 555I=1,N
540 PRINT545,ITM,(SEPAR(I,J),J=1,3),(PCNT(I,J),J=L,3)
545 FORMAT(13,F6.2,F10.2,F10.2,F9.2,F10.2,F9.2)
550 ITM-ITM+IT
555 CONTINUE
556 PRINT 557
557 FORMAT(5X,*-----------------------------------------------------*/)
560 IF(NUMB.EQ.II)575,565
565 II=II+1
570 GO TO 60
575 END
580 ENDPROG
```

REMOVAL OF TOXIC PESTICIDES BY REVERSE OSMOSIS WATER TREATMENT

by

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Bachelor of Science in Mechanical Engineering

University of Massachusetts, 1967

Submitted in partial fulfillment of the requirements for
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1. INTRODUCTION

1.1 STATEMENT OF PROBLEM

The search for new and better methods of removing contaminants from water is becoming increasingly urgent because of the need to provide sufficient potable supplies in the face of rapidly increasing water use. Ready sources of water can be made available in the form of wastewaters from municipalities and industries and contaminated waters from major streams. These waters are often not utilizable without high degrees of treatment, however, because of their contamination with trace organic materials. With increasing demands for water, the goal of much present-day water and wastewater treatment research is to develop methods of producing useful supplies from waters containing such trace organic contaminants.

Standard water treatment processes cannot provide potable water from waste treatment plant effluents containing residual organic and inorganic contaminants in soluble form. Normal water treatment is even inadequate for purifying many heavily polluted river sources.

A number of approaches have been considered over the past several years for improving water treatment methods. Of these, the reverse osmosis process shows great promise because of its relatively low free energy requirement when compared with processes such as freezing and distillation. Thus far, the process has been investigated primarily as a method of desalting sea water, and only recently has any attempt been made to apply reverse osmosis to the treatment of waters containing relatively large amounts of soluble organic as well as inorganic contaminants.

The reverse osmosis method of separating solutes from water by means of a relatively impervious membrane requires merely mechanical energy of pumping the water at high pressure and velocity past the membrane surface. Purified water diffuses through the membrane, leaving the solutes behind in the raffinate. The process although technically feasible, requires much research before it can be utilized economically for water and wastewater treatment.

Of special concern in this research is the presence in water of trace quantities of organic materials such as chlorinated hydrocarbon pesticides. These pesticides are highly insoluble and are thus found in very small concentrations in the natural environment. Although trace in quantity these organics must be removed from water supplies used for domestic purposes. To date few safe and economical methods have been developed for removing trace concentrations of unwanted organic materials from water supplies. On the basis of field applications of the relatively crude reverse osmosis systems developed to date, their future application in removing trace organics from drinking waters is indicated.

1.2 PURPOSE

The purpose of this study was to determine the feasibility of removing trace organic contaminants, particularly the chlorinated hydrocarbon pesticide lindane, from water by utilizing a cellulose acetate membrane and low water pressure.

Pure compounds of known low molecular weight organic materials were utilized to determine the effects of molecular weight, size, and geometrical configuration on the rejection efficiency with a cellulose acetate membrane. Research studies indicating whether cellulose acetate membranes were capable of removing trace concentrations of these potentially dangerous contaminants from water supplies have not thus far been reported in the literature.

1.3 SCOPE

The scope of this study was to accomplish the following:

1. Determine the relationship between pressure, temperature, and water flux rate for an Abcor HFA-100 cellulose acetate membrane, utilizing pressures varying from 30 to 50 psi and temperatures from 24 to 35°C.

2. Measure chemical concentrations in permeate and raffinate for compounds utilized in the study. The chemical compounds utilized were alkyl benzene sulfonate, lindane (gamma isomer of benzene hexachloride), and pentachlorophenol.

3. Utilize the data collected to determine the per cent

rejections of the various compounds over a range of concentrations at 30 to 50 psi.

4. Relate the results of these studies and experiments by others to determine the effects of size, weight, and molecular shape of the compounds on their removal by the membrane process.

2. LITERATURE REVIEW

2.1 PESTICIDE CONTAMINATION OF WATER SUPPLIES

Prior to World War II, pesticides used to control unwanted insects and plants were primarily inorganic in nature. Arsenic, mercury, lead, and plant derivatives were used in the composition of these pesticides (1). Many of these poisons were not specific to individual insects or plants, and they constituted a danger to handlers and consumers.

The compound DDT was the first organic pesticide to come into common use. It was first synthesized in 1874 by Ziedler and approximately fifty years later, Swiss entomologists discovered its insecticidal properties (2). During World War II it was introduced to the American market. The war was highly instrumental in accelerating the use of DDT in order to kill disease-carrying arthropods and food destroying insects. With the increased problems of epidemic control among troops and refugees and the added burden of food demands placed on American farmers, this compound is credited with having done more to alleviate disease and hunger than any other man-made chemical (1). Warrell (3) credited pesticides with saving five million lives, preventing 100 million illnesses, increasing the yield of crops 10 to 20 per cent, and bettering the quality of crops in ten years of use. Secondary benefits, such as the expansion of disease-free land for agriculture and human habitation and increased productivity of people due to better health, can also be credited to pesticides.

The product DDT, in chemical nomenclature:

1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane (4),

can take a number of isomeric forms depending on the position of the substituted chlorine atom. Technical grade DDT is primarily composed of three isomers. The para-para isomer is most active in insecticidal properties and is the major component of technical grade DDT. The para-para isomer is shown below (5).

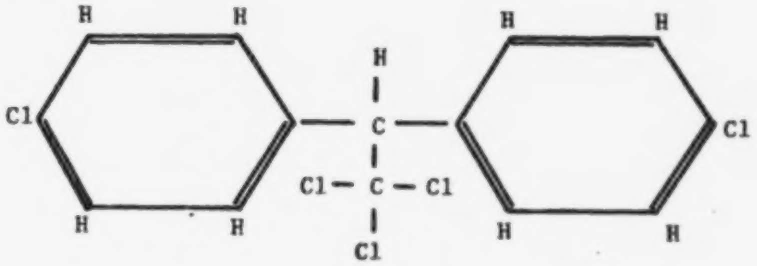


Fig. 1 DDT P,P'-ISOMER

It can be seen that DDT, a typical chlorinated hydrocarbon pesticide, is a relatively small-sized molecule with a molecular weight of 354.5. This molecular weight may be compared with that of sugars, proteins, and other water contaminants, which have molecular weights of several thousand.

Since the Second World War a great many other organic pesticides have been formulated and discovered. The President's Report, entitled:

"Use of Pesticides" (6), stated that as of June 1962, almost 500 compounds incorporated in more than 54,000 formulations were registered for use in the United States. In this same report it was estimated that 350 million pounds of insecticides alone were used and one-twelfth of the land area of the United States was sprayed in 1962. Shepard (7) gave the total production of pure compounds in 1967 as one billion pounds, which was formulated into one and a half million tons of commercial preparations. Nicholson (8) estimated that 92 million acres a year are treated with pesticides. These statistics show the magnitude of the problem confronting Environmental Engineers who must determine the effects of these compounds on the environment.

Pesticides currently in use can be classed into the following general categories: natural organic, chlorinated hydrocarbons, organic phosphates, organic thiocyanates, organic sulphur, thiocarbamates, and inorganic chemicals. The chlorinated hydrocarbon pesticides are popular because of their relatively low human toxicity in contrast to their high insect toxicity. The toxicity of chlorinated hydrocarbons to rats as test animals is shown on the following page in Table 1 (9).

TABLE 1

ACUTE TOXICITY OF SELECTED CHLORINATED HYDROCARBON PESTICIDES

Compound	Oral LD_{50}(mg/kg)	Dermal LD_{50}(mg/kg)
endrin	12.6	75
dieldrin	46.0	75
aldrin	49.5	98
toxaphene	85.0	927
lindane	89.5	950
DDT	114.5	2510
heptachlor	131.0	222
chlorodane	382.5	765
TDE(DDD)	3400.0	---
methoxychlor	6000.0	6000

In contrast, the phosphate compounds, which were originally developed for warfare, are extremely toxic to humans. Their toxicity to rats is shown in Table 2 (9).

TABLE 2

TOXICITY OF SOME COMMONLY USED PHOSPHATE PESTICIDES

Compound	Acute Oral Toxicity (mg/kg)	Acute Dermal Toxicity (mg/kg)
TEPP	1.5	2.4
Phosdrin (mevinphos)	4.9	---
parathion (niron, stathion)	8.3	13.9
methyl parathion	19.0	67.0
EPN	21.8	128.0
malathion	480.	4444.

The phosphate compounds are not as persistent in the environment as are the chlorinated hydrocarbon pesticides. They generally decompose chemically in a matter of days to weeks, while toxic residues of chlorinated hydrocarbons have been found to persist for years. Because they are less dangerous to humans the chlorinated hydrocarbons are more popular than are the organic phosphorus compounds. Nine chlorinated pesticides make up 60 per cent of the United States consumption of these compounds (10). These compounds are DDT, endrin, dieldrin, DDD, DDE, aldrin, heptachlor, heptachlor epoxide and benzene hexachloride.

In a study of water resources it is natural to concentrate on chlorinated hydrocarbons because of their extensive usage and their persistence in the natural environment. DDT has been most extensively studied and may be the most persistent of the common chlorinated hydrocarbon pesticides. Wheatley (11) listed the half life of DDT as 25-40 years while lindane has a half life of only 15-20 weeks. Brooks, et al (9) stated that up to 95 per cent of the originally applied DDT was recovered from the soil after 18 months. Thus, the forces of nature cannot be relied upon to dissipate DDT, and even short duration compounds like lindane persist long enough to cause problems in water resources.

Okey, et al (12) discussed the reason for this persistence. The position of the substituted chlorine atoms have a profound effect on the stability of the compound. Chlorine is strongly electro-negative and draws electrons from the remainder of the molecule to itself (inductive effect). In addition, the chlorine radicals tend to alter the resonant properties of the aromatic compounds, thus altering the electron density at various points in the molecule (mesomeric effect). Alteration of the electron density affects the activation energy of the compound.

Although persistent, the chlorinated hydrocarbon pesticides are quite insoluble in water. Buescher, et al (13) gave the solubilities of aldrin as .02 ppm and lindane as approximately 8 ppm.

The low human toxicity combined with the low solubility of chlorinated hydrocarbon pesticides seem to rule out the possibility of acute poisoning of humans by contaminated water supplies. However, health officials are concerned about possible long term chronic effects of pesticides even in trace quantities.

Although apparently safe for humans, the concentration of pesticides in the environment, especially water, is not always safe for aquatic organisms and wildlife. As a general rule wildlife is sensitive to pesticides in the following order of decreasing sensitivity: fish, amphibians and reptiles, birds, and mammals (6). Some marine organisms have been experimentally poisoned by as small a concentration as 0.9 ppb of heptachlor (6). Aquatic organisms are apparently sensitive to pesticides because of the great volumes of water which pass through their systems. Even at so-called safe biological concentrations, dieldrin was found instrumental in cutting down swimming speed and increasing oxygen uptake of fish (14).

Although chlorinated hydrocarbon pesticides are quite insoluble in water, they are readily soluble in the oils of fish and fats of mammals. There is a tendency for pesticides to concentrate in living organisms through extraction from water. In Clear Lake, California, a case was documented that showed the concentration of TDE to increase from .02 ppm in water to 5 ppm in plankton to 100 to 1,000 ppm in the oil of fish. This concentration proved fatal to grebes subsisting on the fish (6). A study was conducted (6) of the toxicity of DDT to humans. Adult, male volunteers were fed up to 35 mg of DDT per day. Although no ill effects were noticed over a period of 18 months, it was found that DDT became concentrated to up to 270 ppm in the fatty tissues of their bodies. The concentration of DDT in the fat cells of the average adult American who does not receive occupational exposure to DDT, is 12 ppm (6). The concentration of pesticides in fish and mammals is considered a potential source of human poisoning.

It is unfortunate that pesticides cannot be applied specifically where needed and maintained within certain geographic boundaries. In the usual case they tend to disperse throughout the environment with the passage of time. Disposal is dependent on natural conditions as well as on means of application and nature of the compound. Airplane spraying or dusting is a popular means of application due to its speed and economy. In 1958, 22 per cent of the total acreage sprayed in the U.S. was by airplane (15). Spraying and dusting by airplane suffers from wind drift and imprecise control due to the speed of application. Power companies have begun using vacationing students with back-pack sprayers to clear their power lines because of the lack of control in airborne applications.

The chlorinated hydrocarbon pesticides have an attraction for mineral and organic colloids in the soil and particularly for montmorilonite clay (16). Thus erosion of soil will carry pesticides into water courses where these compounds may be carried downstream with the sediments, settle in deposits, or be slowly released from the soil into the water.

Long distance air transport has been recorded for pesticides. In January, 1965, a dust storm blew up in the Southwest United States, and days later a drizzle fell on Cincinnati carrying the dust from the Southwest earthward. The water was found to contain 1.3 ppm organic chlorine and 0.5 ppm organic phosphates. The following individual pesticides were detected: DDE, DDT, chlorodane, heptachlor epoxide, nonnel, dieldrin, and 2,4,5-T (17). Weibel, et al (18) conducted a controlled test in which a field was treated with 2,4-D ester and S-triazine. Both pesticides were detected in precipitation downwind of the application. It was concluded that either the pesticides were transported with soil particles or in the vapor state.

When dealing with pesticides applications, the human factors of carelessness, ignorance, and/or maliciousness must be considered. In the Flint Creek, Alabama, study (8) a case was reported in which a factory discharged parathion, an organic phosphate, into a stream with a flow of 7,000 cfs. This discharge resulted in fish kills a hundred miles downstream. The concentration of parathion in the oil of dead fish varied from 0.75 to 1.5 ppm.

The extensive use of pesticides has led the Federal Government and various researchers to conduct surveys of the extent of pesticide pollution of the environment. The Public Health Service in October, 1957, implemented Public Law 660 (19), establishing a surveillance system in which the PHS was authorized to collect and disseminate basic data on chemical, physical, and biological water quality as related to water pollution control. A total of 131 stations were established to collect this data. The PHS (20) detected the following pesticides in a study of the ten major streams in the country: dieldrin, endrin, DDT, and DDE in all ten streams; heptachlor and aldrin in some of the streams; DDD in one sampling station; and presumptive evidence of benzene hexachloride. The PHS (8) also conducted a regional study of the Flint Creek, Alabama, watershed. By limiting the study to a single watershed various parameters were more accurately monitored.

Steps to control pesticides have taken various forms. Immediate steps without technical development include: the Federal monitoring system, a program of control on the permissible use of pesticides, regulations on the labeling of pesticides containers, and educating the users of pesticides on the dangers and proper handling of the compounds. The Federal Committee on Pest Control (21) has been set up to coordinate efforts in this area and it published a Pesticides Monitoring Journal (12) to keep the population informed on pesticide problems.

Alternatives to the use of pesticides frequently require more time since technical and agricultural developments may be necessary (6). Some of these methods include the following: use of areas inhospitable to pests, movement and rotation of crops to leave pests behind, planting in a season that is low in pests, use of disease resistant crops, alteration of the environment; i.e. drainage of swamps, and utilization of the natural enemies of pests. Techniques requiring development include irradiation of insects to cause sterility and the use of sex attractants to lure males to their deaths (6).

Research has been conducted to determine the effectiveness of water treatment methods in removing pesticides. Standard water treatment methods have been found to be economically or technically unfeasible. Activated carbon can remove relatively high percentages of some organic compounds, but its application is considered uneconomical because of the massive dosages required to remove the last remaining amounts of organic matter at the lower concentrations. Chemical coagulation, sedimentation, rapid sand filtration, and standard chlorination practices resulted in low removals of most normal pesticides in water (13, 22).

2.2 REVERSE OSMOSIS

2.2.1 HISTORY OF REVERSE OSMOSIS

Because of the generally unsatisfactory results obtained using standard water treatment techniques for pesticide removal, a search was made for new techniques (13, 22). Researchers working on saline water conversion have already investigated three major new concepts in water purification. These techniques are: freezing, distillation and reverse osmosis. Reverse osmosis has the greatest potential in the area of brackish water and wastewater purification. This popularity is due to the relatively small demand in energy of reverse osmosis in comparison to the other methods. Freezing and distillation both require energy for a change of phase and both operate at temperatures other than ambient. In contrast, reverse osmosis requires no phase change and wastes little energy by heat transfer. Also the separation problem is thought to be less in reverse osmosis than in the other methods. In freezing, the brine and ice form a uniform slurry which is generally separated by washing the brine off the ice. This obviously sacrifices water for washing and results in some ice melting. In distillation, the separation of volatile substances is considered to be a problem. Also, both freezing and distillation derived little benefit from a decrease in concentration, while in reverse osmosis a low concentration contaminant can be more easily removed than a high concentration (23, 24).

The phenomenon of osmosis was first observed in 1748 by Abbe Nollet while he was conducting research on biological membranes. He noted that when two solutions of the same composition, but at different concentrations were separated by a semi-permeable membrane, a flow of solvent would occur from the concentrated to the dilute solution (25, 26). The first experiments with artificial membranes were prepared during the mid 19th century by precipitating copper ferro-cyanide into the pores of porcelain (26). Also, during the 19th century Pfeffer made the first direct measurements of osmotic pressure. In 1886, Van't Hoff used Pfeffer's data to prepare a theory of solutions (25, 26).

Early work on the phenomenon of osmosis centered on membranes permeable to water but relatively impermeable to alcohol, sugars, and compounds of still higher molecular weights. However, it was recognized that permeabilities of different salts in solution varies. During the first half of the 20th century, Teorell and Sollner carried out extensive research on salt permeability (27, 28).

Interest in osmosis declined after the 1920's until 1953, when a program was undertaken at the University of Florida under the direction of Professor C. E. Reid. This program was supported by the Office of Saline Water in the United States Department of the Interior and sought to find a membrane suitable for the separation of fresh water from seawater. Reid and his co-worker Breton found that a cellulose acetate film made a suitable membrane for use in the separation of water and salt employing the reverse osmosis process. Unfortunately, this membrane, presently called the normal cellulose acetate membrane, did not exhibit a sufficiently high flux rate for practical applications (29, 30).

Loeb and Sourirajan (31) developed a modified cellulose acetate membrane at UCLA in 1960. This film not only exhibited the high selectivity of the normal membrane but also allowed practical water flux rates. The development of the modified membrane has encouraged further research in the field of reverse osmosis.

Since the pioneering work of Reid and Loeb, a great many studies have been made to develop membrane systems which would continue to exhibit high flux rates consistent with high rejection efficiencies. Research has also been conducted to improve the cellulose acetate membrane, including the development of fabrication techniques for ultrathin membranes (32); ways to plug defects in the modified membrane (33); and methods of manufacturing non-compacting membranes (34). Not all of these endeavors have been completely successful. Another field of study is the search for better materials for the composition of the membranes (26).

2.2.2 PRINCIPALS OF REVERSE OSMOSIS

The principals of osmosis and reverse osmosis are illustrated in Fig. 2. It is well known that the chemical potential or activity of a solvent decreases with the addition of a solute. Thus, distilled water will have greater chemical potential than a water solution containing a salt. If two solutions of different concentrations under equal pressure are separated by a semi-permeable membrane, the greater chemical potential of the dilute solution will cause a flow of solvent through the

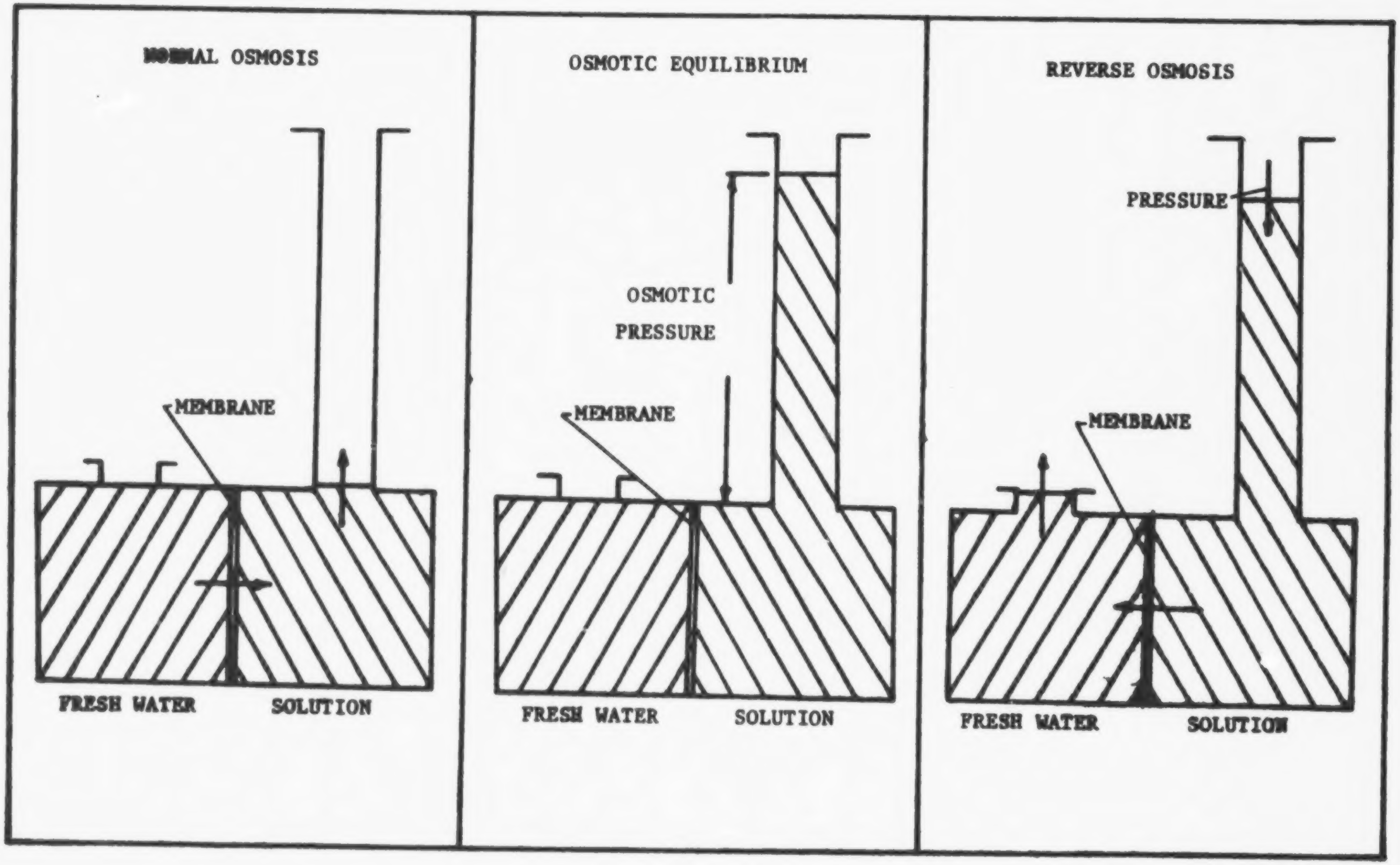

NORMAL OSMOSIS
MEMBRANE
FRESH WATER
SOLUTION
OSMOTIC EQUILIBRIUM
OSMOTIC
PRESSURE
MEMBRANE
FRESH WATER
SOLUTION
REVERSE OSMOSIS
PRESSURE
MEMBRANE
FRESH WATER
SOLUTION

Fig. 2 SCHEMATIC DIAGRAM OF REVERSE OSMOSIS

membrane from the dilute solution to the concentrated solution. This process is referred to as osmosis. The membrane is semi-permeable because it permits the flow of solvent, but stops most solute molecules. To be precise, reverse osmosis refers to the passage of only solvent, while solute is retained. However, it has been used in a liberal definition in this work to describe transport which include both solvent and solute flow. Other investigators sometimes refer to this combined flow as ultrafiltration or hyperfiltration.

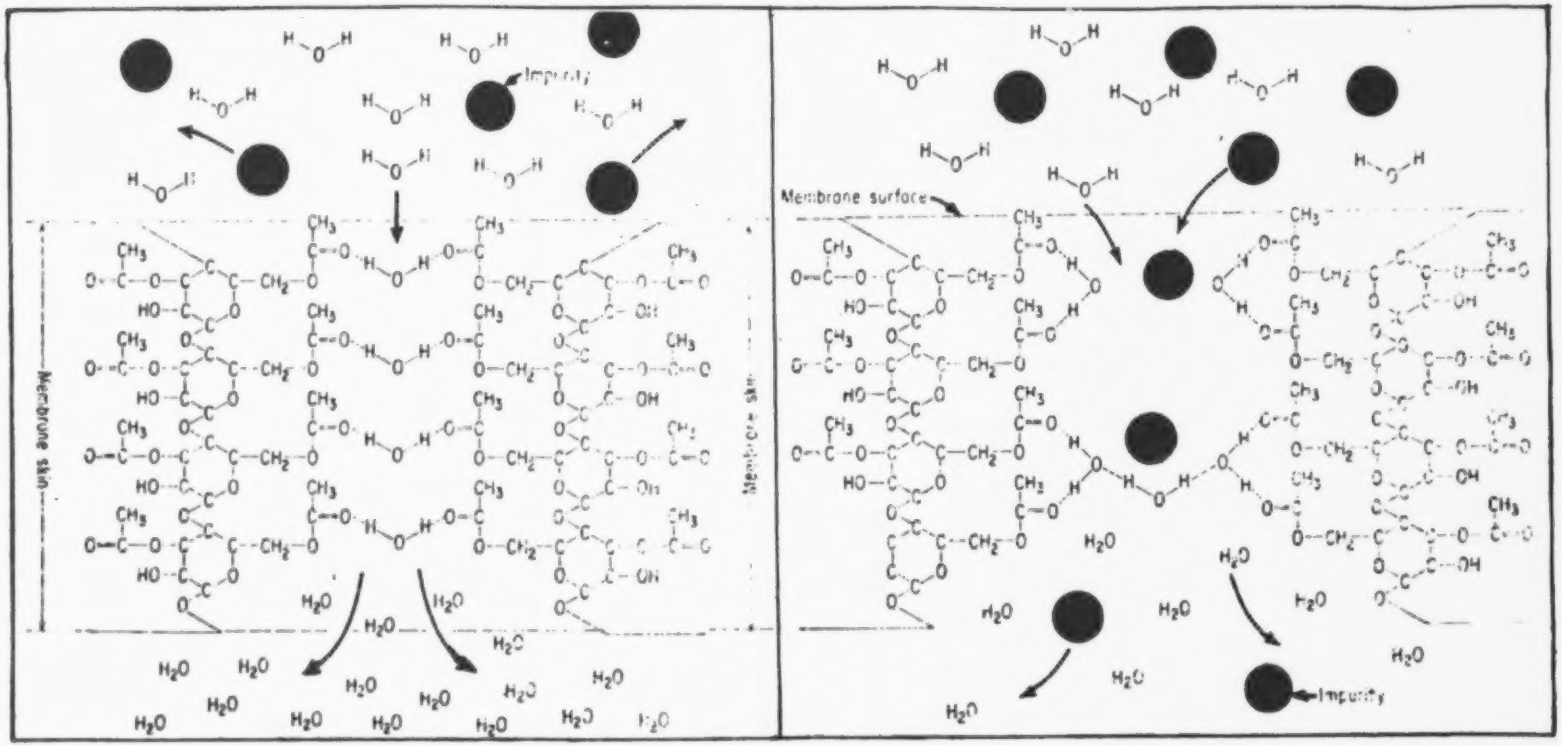
Pressure as well as concentration affects the chemical potential of a solution. Thus, as water flows from the dilute to the concentrated solution side of a membrane, the increase in water head on the concentration side, as well as the decrease of concentration, will act to decrease the difference in chemical potential between the two solutions. Eventually an equilibrium will be established between the two solutions. At this point, the water head on the concentrated side of the membrane will balance the chemical potential difference between the two solutions. This head is known as osmotic pressure.

In reverse osmosis, flow is forced in a direction opposite to that which would normally occur in regular osmosis. This is accomplished by applying pressure to the concentrated solution to increase its chemical potential to the point that the concentrated solution has a higher chemical potential than the dilute solution. The applied pressure which is required to equilibrate the chemical potential of the two solutions is the osmotic pressure. The mechanism by which water passes through the collulose acetate membrane has been a source of controversy since the development of this membrane. One highly popular theory (35) suggests that water is transferred from one absorption site to the next under the influence of a pressure gradient. Fig. 3 illustrates the assumed (36) structure of the membrane skin where the majority of the separation is said to occur. This skin consists of a series of polymer chains which are cross-linked at their ends by water molecules. The water molecules are bonded to carbonyl oxygen atoms by hydrogen bonding. These amorphous gaps between the chains can be small or large. The gaps are considered small if one water molecule is adequate to cross-link the chains. In these small gaps, the water links can be displaced under the influence of hydraulic pressure by water molecules from the solution. In this way water molecules diffuse through the membrane by so-called allignment type diffusion. Dissolved solids as ions or molecules cannot pass through this tight structure.

Large gaps between polymer chains require a bridge of several water molecules to link the chains together. Bonds between water molecules are considerably weaker than bonds between water molecules and carbonyl oxygen molecules. The larger space and increased weakness of these larger gaps permits solute flux through the membrane under the influence of a concentration gradient.

A similar theory (26) states that water flows through the matrix itself under the influence of pressure. Solute flux is concentration dependent and occurs through both the matrix and defects.

Sourirajan (37) has proposed that compounds are selectively absorbed by the membrane. In the case of NaCl, salt, negative absorption of the


Impurity
Membrane skin
Membrane surface
Impurity

Alignment type diffusion allows the passage of pure water only

Hole type diffusion allows the passage of impurities as well as water

Fig. 3 SCHEMATIC MOLECULAR DIAGRAMS OF THE MEMBRANE SKIN (36)

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salt occurs and develops a salt-free layer adjacent to the membrane. It is this negative absorption which accounts for the selectivity of the cellulose acetate membrane. Thus, a pure layer is forced through pores in the membrane by the pressure gradient existing across the membrane. These pores in the membrane result from the leaching of electrolytes from the surface during preparation. The actual size of the pores, which will determine the amount of salt which will pass through, can be controlled by the temperature of the water bath during annealing of the membrane.

2.2.3 MATHEMATICAL MODELS

Mathematical models have been proposed to explain the transport process in reverse osmosis. The transfer of solute and solvent through the membrane is based on chemical equilibrium across the membrane (25). When two aqueous solutions of a single salt, both at the same temperature, T, and at pressures P_1 and P_2, are separated by a semipermeable membrane, the chemical potential difference for water, $\Delta\mu_w$, across the membrane is given by:

$$\Delta\mu_w = \int_{P_1}^{P_2} \left(\frac{\delta\mu_w}{\delta P}\right)_{N_s,T} dP + \int_{N_{S1}}^{N_{s2}} \left(\frac{\delta\mu_w}{\delta N_s}\right)_{P,T} dN_s \qquad (1)$$

N_{s1} = Mole fraction salt on the high pressure side of the membrane

N_{s2} = Mole fraction salt on the low pressure side of the membrane

Assuming that the partial molar volume of water, $\overline{V}_w$, is pressure independent in the range of interest, Eq. 1 becomes:

$$\Delta\mu_w = \overline{V}_w \Delta P + \int_{N_{s1}}^{N_{s2}} \left(\frac{\delta\mu_w}{\delta N_s}\right)_{P,T} dN_s \qquad (2)$$

ΔP = Pressure difference between the two solutions.

For the chemical potential across the membrane to be equal, the pressure difference must be equal to the osmotic pressure. The equation then reduces to:

$$\int_{N_{s1}}^{N_{s2}} \left(\frac{\delta\mu_w}{\delta N_s}\right)_{P,T} dN_s = -\overline{V}_w \Delta\pi \qquad (3)$$

$$\Delta\mu_w = \overline{V}_w (\Delta P - \Delta\pi) \qquad (4)$$

$\Delta\pi$ = change in osmotic pressure

Eq. 3 forms the basis for most determinations of osmotic pressure which are made experimentally. The chemical potential of a solvent is measured as a function of its concentration, usually through vapor pressure measurements. The osmotic pressure can then be calculated using the integral in Eq. 3.

For dilute solutions obeying Raoult's Law, one may write:

$$\mu_w = \mu^{\bullet}_w + RT\ln N_w \simeq \mu^{\bullet}_w - RTN_s \qquad (5)$$

$\mu^{\bullet}_w$ = chemical potential of the pure solvent

When Eq. 3 and 5 are combined together a limiting expression for the osmotic pressure of a solution is derived:

$$\pi = \frac{RTN_s}{\overline{V}_w} \qquad (6)$$

Using thermodynamics (25) the theoretical minimum work for separation of solute and solvent can be derived. This theoretical minimum will be the same no matter what method of separation is employed. Assuming that the work, W, across the membrane is reversible, its value per mole of water removed from the concentrated solution is the product of pressure difference across the membrane and the volume of water passed through the membrane. Under reversible conditions the pressure drop across the membrane is the osmotic pressure, and the volume per mole of water is the molar volume.

$$W = \Delta\pi\overline{V}_w \qquad (7)$$

The minimum theoretical work for removing water from seawater, 33,000 ppm NaCl, has been calcualted to be 0.74 Kwhr/m^3. To achieve practical flux it has been estimated that approximately 5 Kwhr/m^3 would be required. In terms of heat requirement, this equals a demand of 12,000 kcal/m^3, assuming 35% efficiency in converting from heat to mechanical energy. In contrast a distillation plant at Pt. Loma, California, requires 56,000 kcal/m^3 (38). Thus, a reverse osmosis system requires much less energy than a distillation system.

2.2.3.1 SOLUTION DIFFUSION TRANSPORT MODEL

The actual mechanism of transport across the membrane has been put into mathematical form. The most commonly used model for the membranes exhibiting high salt rejection is the solution diffusion model. A boundary layer is established due to the flow of water across the surface of the membrane in most membrane systems. In this boundary layer the concentration of salt will build up due to the selective transport of water through the membrane. Since the salt flow through the diffusion region is small, water flow can result only from a gradient of chemical potential for the water (25). In general, the difference in chemical potential across the membrane is small enough so that the gradient in the equations can be replaced by a difference in chemical potential of water between the two sides of the membrane divided by the membrane thickness, ΔX. Thus Eq. 4 for water flux becomes:

$$F_w = -\alpha \text{ grad } \mu_w \simeq -\alpha \bar{V}_w \frac{\Delta P - \Delta \pi}{\Delta X} \tag{8}$$

α = Permeability parameter

In the viscous flow region Poiseuille flow is assumed and the viscous flow equation becomes:

$$F_w = -\beta \frac{\Delta P_v}{\Delta X_v} \tag{9}$$

β = viscous permeability parameter

ΔP_v = pressure drop across the viscous flow region

ΔX_v = thickness of the viscous flow region

Combining Eq. 8 and 9, the complete flow equation is obtained:

$$F_w = - \frac{\alpha \bar{V}_1 \beta}{\alpha \bar{V}_1 \Delta X_v + \beta \Delta X} (\Delta P_T - \Delta \pi) \equiv A(\Delta P_T - \Delta \pi) \qquad (10)$$

ΔP_T = total pressure drop across the membrane

A = total permeability parameter

This equation can be further considered using diffusion and solubility coefficients. If the validity of Henry's and Fick's Laws in the water-cellulose acetate solution is assumed, the result is:

$$F_w = - \frac{D_w C_w \bar{V}_w}{RT} \left(\frac{\Delta P - \Delta \pi}{\Delta X}\right) \qquad (11)$$

C_w = water concentration in the cellulose acetate

D_w = diffusion coefficient for water in the membrane

R = gas constant

The solubility of water in cellulose acetate is found by using an absorption test which determines the weight the membrane will gain in soaking. The solubility for water in a 39.8% acetyl content membrane is 0.16 g/cc of wet cellulose acetate. The quantity $D_w C_w$ is determined by osmosis experiments. When one solution is 5% sodium chloride and the other is distilled water, the quantity equals 2.6 x 10^{-7} g/cm-sec. This same value was derived using reverse osmosis at applied pressures of 1500 psi. Thus, the diffusion coefficient can be calculated to be 1.6 x 10^{-6} cm^2/sec. This diffusion coefficient compares favorably with the self diffusion coefficient for water in the liquid state, which was given by Wang (39) to be 2 x 10^{-5} cm^2/sec at 25°C.

If the salt flow through the diffusion barrier is assumed to be independent of water flow, the salt flux, F_s, may be written:

$$F_s = -\alpha_s \text{ grad } \mu_s \simeq \alpha_s \left(\frac{\delta\mu_s}{\delta C_s}\right)_{P,T} \text{ grad } \rho_s \qquad (12)$$

$$F_s = -\alpha_s \left(\frac{\delta\mu_s}{\delta C_s}\right)_{P,T} \frac{\Delta\rho_s}{\Delta X} \equiv -B\Delta\rho_s \qquad (13)$$

F_s = salt flux

α_s = permeability factor for salt

μ_s = salt chemical potential

ρ_s = salt concentration in the solution

B = salt permeation constant

The pressure effect on the chemical potential of the salt was assumed to be minor compared to the effect of concentration. Fick's Law was also assumed to apply in the diffusion barrier. Thus, it is seen that salt permeation is proportional to the difference in the salt concentration across the membrane. This equation is usually stated as follows:

$$F_s = -D_s K \frac{\Delta\rho_s}{\Delta X} \qquad (14)$$

D_s = diffusion coefficient for salt in the membrane

K = distribution coefficient for sodium chloride between the membrane and the external solution.

The distribution coefficient is independent of concentration and is found to be 1 to 10 wt-% sodium chloride in the external solution. The diffusion coefficient for sodium chloride is approximately 9.4×10^{-10} cm^2/sec.

2.2.3.2 VISCOUS FLOW TRANSPORT MODEL

Other models have been proposed and the most popular of these is the viscous flow model (40). Generally, this model is used in correlation with high permeability, low salt rejection membranes. This model allows for coupled flow and limits flow to pores rather than diffusion through the membrane.

Thus, the total volumetric flow through the membrane is described using Poiseuille's Law:

$$\varepsilon u = -H \frac{dP}{dy} = -\frac{\varepsilon r^2}{8\eta} \frac{dP}{dy} \tag{15}$$

ε = fractional open area of the membrane

u = center of mass velocity of the pore fluid (cm/sec)

H = Hydrodynamic permeability of the membrane (cm^2/sec-atm)

P = pressure (atm)

y = direction perpendicular to the membrane surface

r = equivalent cylindrical pore radius (cm)

η = viscosity of the pore fluid (atm-sec)

The pressure gradient was replaced because the viscosity and pore radius were assumed to remain constant through the thickness of the membrane. Thus, the pressure gradient was replaced with a change in pressure across the membrane divided by the length of the pores through the membrane.

$$\varepsilon u = -\frac{\varepsilon r^2}{8\eta}\frac{\Delta Pm}{t\lambda} \qquad (16)$$

ΔPm = fluid pressure drop in the membrane

λ = tortuosity factor to account for non-linear pores

t = thickness of the membrane (cm)

In such an equation the salt flow is a sum of the contribution due to bulk flow of the fluid and another due to the diffusion of the solute in the flowing streams:

$$F_s = C_{sm} u + J_s \qquad (17)$$

C_{sm} = solute concentration in the membrane (moles/unit total membrane volume)

J_s = diffusive flow of solute per unit membrane area

Assuming Fick's Law applies, the diffusive flux is:

$$J_s = -D_{sw}\frac{dC_{sm}}{dy} \qquad (18)$$

D_{sw} = diffusion coefficient for the solute in the pore fluid.

Combining the above equations, yields:

$$F_s = -D_{sw}\frac{dC_{sm}}{dy} + C_{sm} u \qquad (19)$$

It is quite evident from these equations that salt rejection can only be achieved by a change in concentration between the external solution and the membrane pores. If chemical equilibrium is assumed across the interfaces, the equations are:

$$C'_{sm} = K'\rho'_s \qquad (20)$$

$$C''_{sm} = K''\rho''_s$$

ρ_s = concentration of solute in the pollution

$''$ = high pressure interface

$'$ = low pressure interface

K = distribution coefficient for sodium chloride between the membrane and the external solution.

Integrating Eq. 19 yields:

$$C_{sm} = \frac{F_s}{u} + B \exp\left(\frac{u}{D_{sw}} y\right) \qquad (21)$$

B = intergration constant

In reverse osmosis experiments appropriate boundary conditions are that the equations for C'_{sm} and C''_{sm} are satisfied at $Y = 0$ and $Y = -t$ and that $F_s/eu = C''_s$. (22)

This last expression indicates that the product concentration is determined by the relative magnitudes of the salt and water flows through the membrane.

Thus, the permeate concentration is:

$$\rho''_s = \frac{K'C'_s \exp\left(-\frac{ut\lambda}{D_{sm}}\right)}{K'' - \varepsilon + \varepsilon \exp\left(-\frac{ut\lambda}{D_{sm}}\right)} \qquad (23)$$

ρ''_s = solute concentration permeate

It is apparent in Eq. 23 that the lowest product solute concentration is achieved at the highest (in the negative y direction) linear velocities, and that in the limit:

$$\frac{\rho'_s}{\rho''_s} = \frac{\varepsilon}{K} \qquad (24)$$

The assumption of chemical equilibrium across the interface requires the chemical potential for water and salt to be continuous across the interfaces. Thus, the pressure in the pores must differ from the external solution by an amount equal to the osmotic pressure difference across the interface.

$$\Delta P_m = \Delta P - \Delta\pi' + \Delta\pi'' \qquad (25)$$

$\Delta\pi'$ = osmotic pressure difference across the low pressure interface

$\Delta\pi''$ = osmotic pressure difference across the high pressure interface

The osmotic pressure differences in terms of concentration differences are given as:

$$\Delta\pi' = RT\left(\frac{C'_{sm}}{\varepsilon} - \rho'_s\right) = RT\rho'_s\left(\frac{K'}{\varepsilon} - 1\right) \qquad (26)$$

$$\Delta\pi'' = RT\left(\frac{C''_{sm}}{\varepsilon} - \rho''_s\right) \approx RT\rho''_s\left(\frac{K''}{\varepsilon} - 1\right)$$

The pressure difference then becomes:

$$\Delta P_m = \Delta P - RT\left[\rho'_s\left(\frac{K'}{\varepsilon} - 1\right) - \rho''_s\left(\frac{K''}{\varepsilon} - 1\right)\right] \qquad (27)$$

This pressure difference may then be used in Eq. 15:

$$\varepsilon u \simeq \frac{\varepsilon r^2}{8\eta t\lambda}\left[\Delta P - RT\left(\rho'_s\left(\frac{K'}{\varepsilon} - 1\right) - \rho''_s\left(\frac{K''}{\varepsilon} - 1\right)\right)\right] \qquad (28)$$

These two mathematical models represent the extreme conditions of either diffusion or pore flow. The actual mathematical model may be a combination or something between the two models. The frictional or facilitated transport model which has been used to explain phenol flow through a cellulose acetate membrane is between these two models (34). Here flow occurs through pores but the pore walls exert a frictional effect on the solute flow.

2.2.4 COMPOSITION AND FABRICATION OF REVERSE OSMOSIS MEMBRANES

Having discussed theories of flow, it is of interest to consider the composition and fabrication of modified cellulose acetate membranes. These membranes are of special interest since they are the most practical membranes developed to date for the treatment of salt or undissociated solutes.

The modified membrane has been examined by electron microscopy and been found to consist of two layers. The first layer is dense and on the order of .25 microns thick. This dense layer is credited with the separation function of the membrane. The remainder of the membrane consists of a porous gel-like structure approximately 100 microns thick. It serves to support the dense skin of the membrane when under high pressures.

The membrane is prepared from a solution typically containing cellulose acetate 22.2% wt, magnesium perchlorate 1.1% wt, acetone 66.7% wt, and water 10.0% wt (26). This solution is poured onto a clean smooth glass plate and the thickness adjusted using a doctor blade. The plate is then submerged in an ice water bath for a period of 30 to 60 minutes. During this period magnesium perchlorate is leached from the membrane. Following this ice bath, the membrane is annealed in a hot water bath for 3 to 10 minutes. The temperature of this bath plays an important role in determining the properties of the membrane. It has been found that from a temperature of 55°C and up, the salt rejection properties of a membrane are improved at the expense of water flux rate.

The balance of acetate to cellulose is also considered critical to the performance of the membrane. A ratio of 2.5 acetate groups to 1 cellulose group is considered optimum for best membrane performance (26). This ratio is achieved by first forming tri-acetate and subsequently hydrolyzing the acetate to a 2.5 to 1 ratio with cellulose. Subsequent hydrolysis is prevented in operation by the maintenance of a pH of 5.5.

Perhaps the only significant difficulty encountered in the use of cellulose acetate membranes is the tendency for the porous supporting structure to compress under a high pressure. This compaction leads to a decrease in solvent flows over a period of time. Efforts have been made to counter this tendency by adding various binder materials to the cellulose acetate to strengthen it.

Other approaches have called for the formation of an ultrathin dense cellulose acetate skin on a porous but strong backing material.

These efforts have included the addition of sand and asbestos to cellulose acetate, porous plastic backings with leachable fillers of salt, and a relatively impervious backing of sintered glass and cement board with grooves cut for fluid transport. In cases where the supporting material has large enough pores or channels to cause the membranes to collapse into them, it has been found that a tight weave cloth, such as nylon, placed over the backing material serves as an adequate support for the membrane (41).

Ultrathin membranes (32) utilizing the improved backing materials are considered a possible solution to the problem of modified membrane flux decline. The fabrication of these membranes requires an extremely smooth and clean glass plate as a drawing surface. By withdrawing a plate from a membrane solution, a film will form on the surface of the plate. This film will form into a dense, highly retentive membrane by air drying and can be removed from the plate without damage by floating it off in water. The thickness of the membrane can be adjusted by varying the speed of withdrawal of the plate from the solution. Researchers have been able to produce two membranes which achieved the maximum theoretical rejection predicted for NaCl of 98.7% (32, 42, 43).

Efforts are being expended to develop other materials for reverse osmosis membranes. Some materials which have shown promise are polyvinylpyrollidone, poly (vinylene carbonate), and graphitic oxide (26).

A development at Oak Ridge National Laboratories (26) of the Atomic Energy Commission by Dr. Kraus and associates has shown promise for extremely high flux rates in reverse osmosis membranes. They prepared a dynamically formed membrane by pumping water containing a hydrous oxide (zinconium or thorium) or a polyelectrolyte (polyvinylbenzyl-trimethyl-ammonium chloride) over a porous backing. The porous structure can have a pore size up to 5 microns in diameter. This combination results in flux rates of 100 to 300 gfd as opposed to 20 to 30 gfd for cellulose acetate modified membranes. However, this membrane permits the passage of polyvalent counterions (Mg^{++} or $SO_4^{=}$) and even breaks down in their presence.

2.2.5 REVERSE OSMOSIS SYSTEMS

With flux rates of 20-30 gfd, it is quite obvious that a large surface area is required for significant water flow. Thus, efforts have been devoted to engineering practical reverse osmosis systems. Four designs have been proposed to meet the requirements of high-water flow in a small volume; flat plate, spiral-wound, tubular and hollow fiber (26).

The flat plate is the simplest and perhaps least efficienc system. It consists of laminates of membrane and porous plates. The applied pressure acts to force solvent through the membranes and into the porous plates and then out the edges or backs of these porous layers. The module used in the experiments was a simple flat plate system with only one membrane and porous layer. This module is shown in Fig. 4.

The spiral-wound configuration was an effort to enlarge the surface area to volume ratio. Sheets of membranes and porous spacers were laminated together and wrapped around a central product water collection pipe with weep holes. Feed water enters along a porous sheet and slowly seeps through the membrane into a second porous layer which conducts the water to the central tube for collection. Because of the slow flow of feed water through the porous laminate there is a concentration build-up adjacent to the membrane surface in this design. The spiral-wound system is illustrated in Fig. 5.

The tubular unit consists of long tubes with a membrane coating on the inside. The solvent passes through the membrane and through weep holes in the tubes. The system adapts itself to easy module fabrication and convenient and rapid module replacement. Fig. 6.

The hollow fiber system is the msot recent approach and realizes a great surface area to volume ratio by the use of fine fibers. As opposed to the tubular unit, flow is from the outside to the inside of the fibers. The large surface area to volume ratio has permitted the use of lower flux, tighter membranes with rejections approaching theoretical values. This system is illustrated in Fig. 7.

A common problem with the last three configurations is the tendency for a high concentration of solute to develop adjacent to the

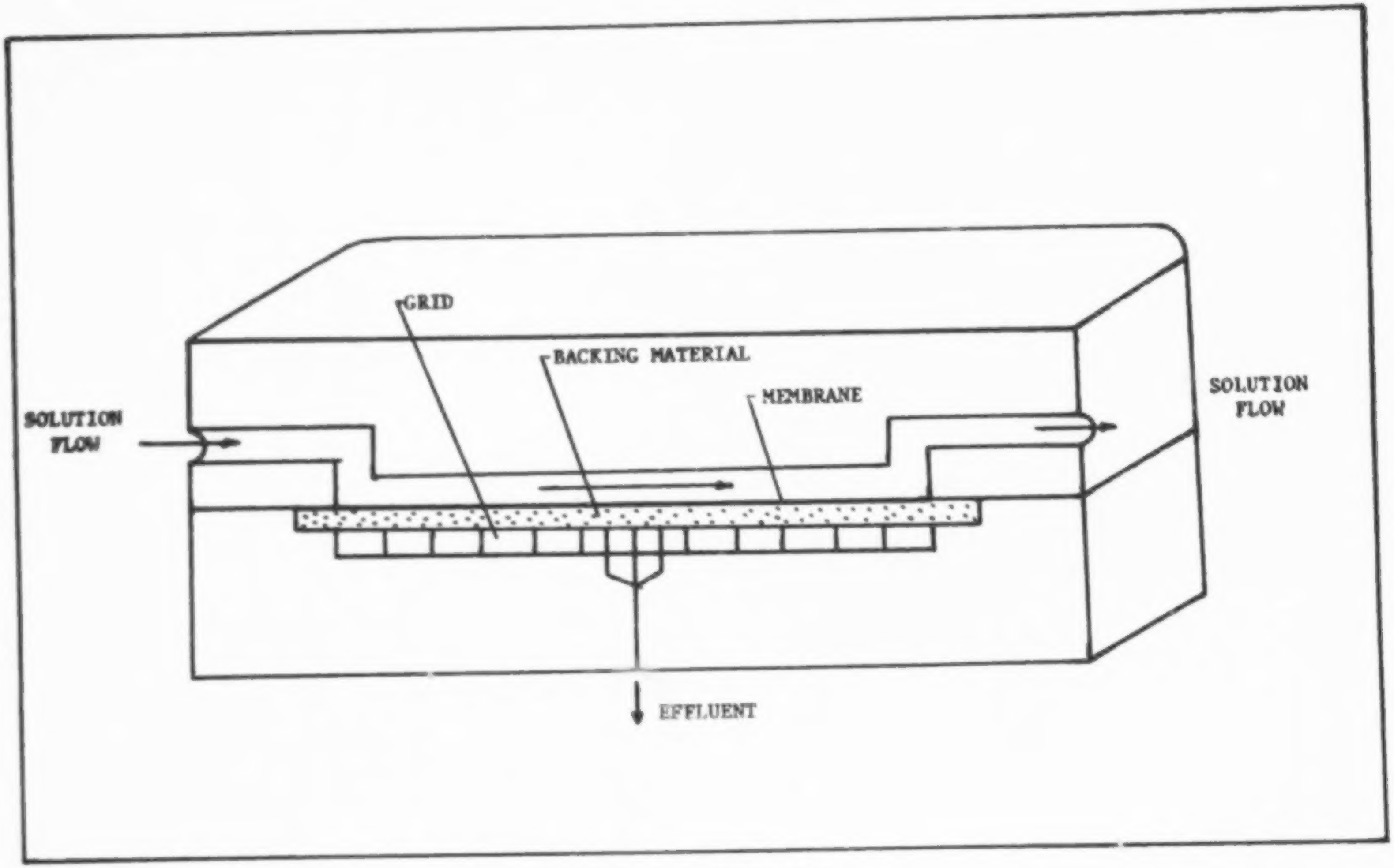
SOLUTION FLOW
GRID
BACKING MATERIAL
MEMBRANE
SOLUTION FLOW
EFFLUENT

Fig. 4 REVERSE OSMOSIS CELL

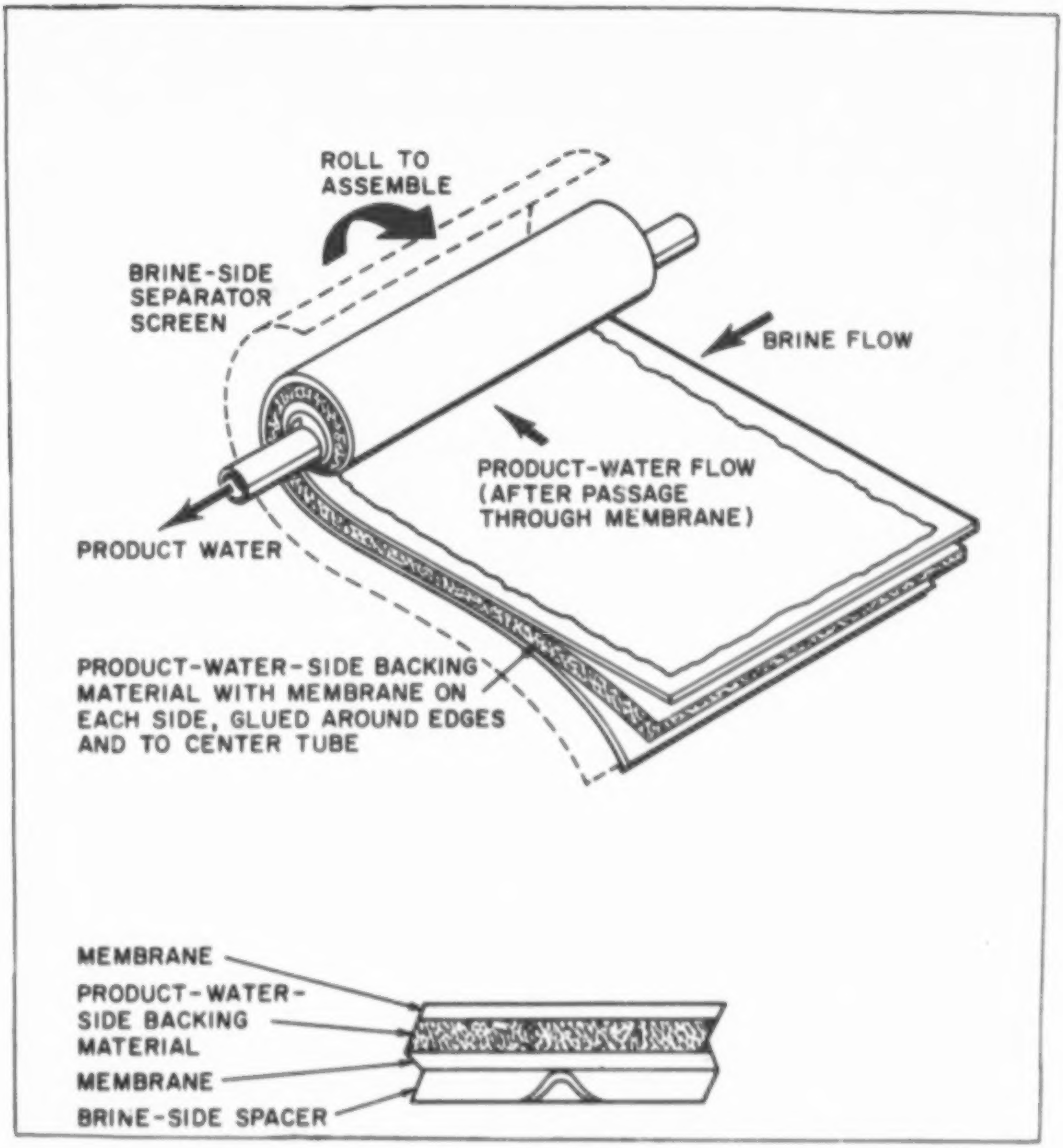
ROLL TO ASSEMBLE
BRINE-SIDE SEPARATOR SCREEN
BRINE FLOW
PRODUCT-WATER FLOW (AFTER PASSAGE THROUGH MEMBRANE)
PRODUCT WATER
PRODUCT-WATER-SIDE BACKING MATERIAL WITH MEMBRANE ON EACH SIDE, GLUED AROUND EDGES AND TO CENTER TUBE
MEMBRANE
PRODUCT-WATER-SIDE BACKING MATERIAL
MEMBRANE
BRINE-SIDE SPACER

Fig. 5 A SPIRAL-WOUND REVERSE OSMOSIS MODULE (26)

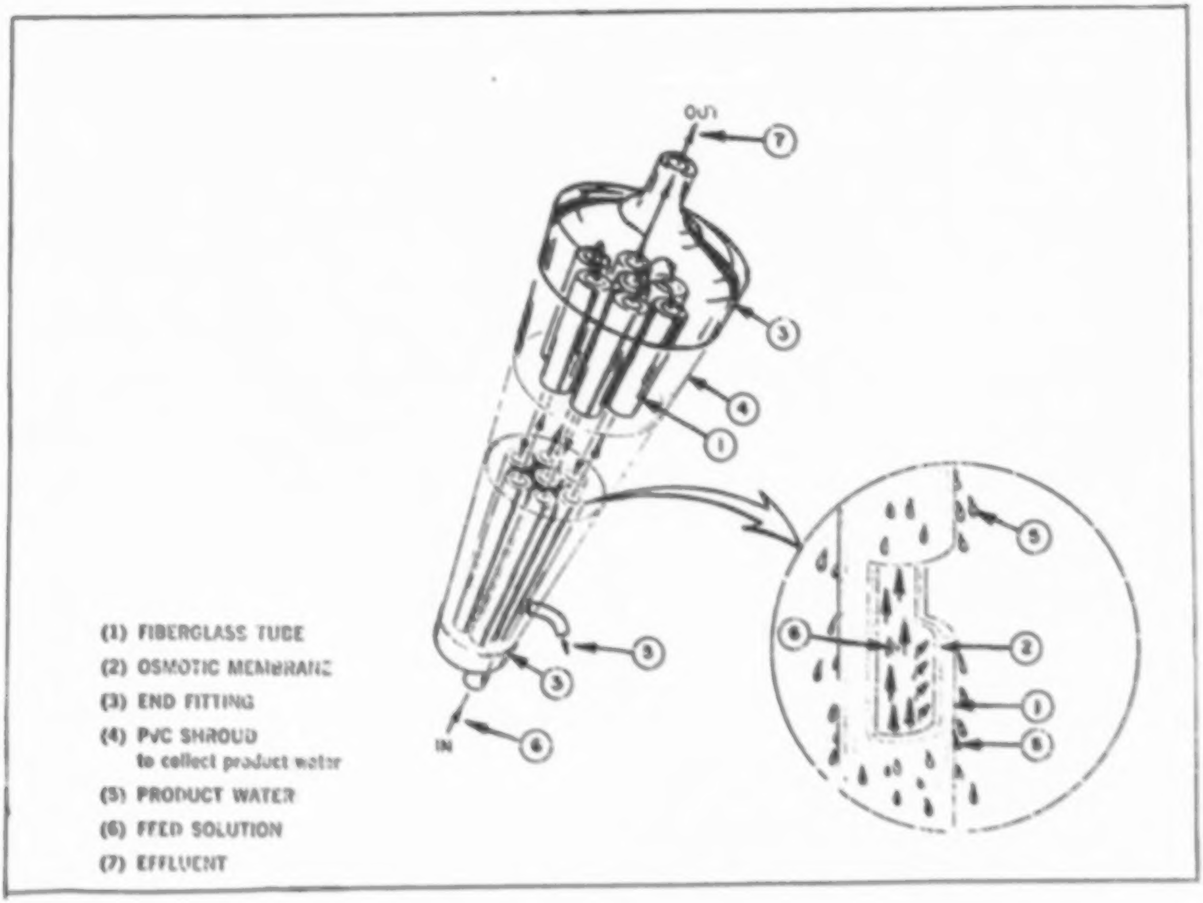
OUT
⑦
③
④
①
⑤
⑥
②
①
⑤
③
③
IN
⑥
(1) FIBERGLASS TUBE
(2) OSMOTIC MEMBRANE
(3) END FITTING
(4) PVC SHROUD
to collect product water
(5) PRODUCT WATER
(6) FEED SOLUTION
(7) EFFLUENT

Fig. 6 A TUBULAR REVERSE OSMOSIS UNIT (26)

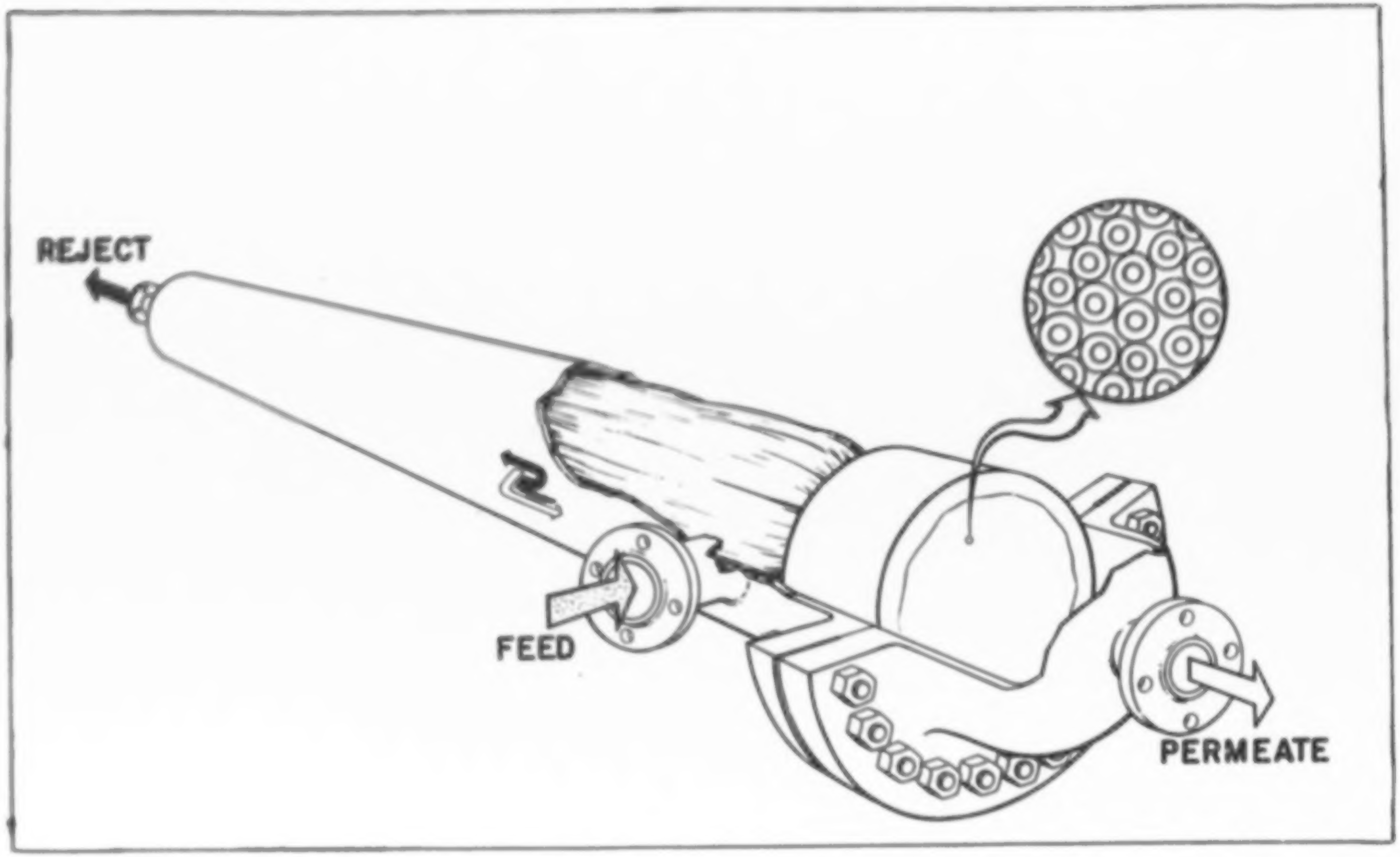
REJECT
FEED
PERMEATE

Fig. 7 A HOLLOW-FIBER REVERSE OSMOSIS UNIT (26)

membrane. Presently, the only practical solution for this concentration polarization problem is to wash the solute off the membrane by maintaining a high water flow rate over its surface. Obviously this isn't possible in the spiral-wound or hollow fiber systems.

2.2.6 REVERSE OSMOSIS FOR WATER RE-USE

Most reverse osmosis research has been in the removal of salt from seawater or brine, and therefore most systems and equations have been developed with NaCl as the solute. In recent years engineers have looked to other untapped sources of water supplies, and it became apparent that waste water is a vast untapped resource. Wastewater generally carries much smaller quantities of dissolved matter than seawater so that wastewater should be easier to purify than seawater.

With this idea in mind, a number of studies have been made in the laboratory to determine the effectiveness of reverse osmosis in handling wastewater. Some companies have carried their experimenting to the pilot plant stage. The following pilot plants have been reported on quite frequently in the literature: Pomona, California; Azusa, Arizona; and Bergen County, New Jersey (44, 14, 45).

The Pomona test (44) was the first in which a practical membrane system was applied to wastewater for an extended period of time. The system employed a spiral-wound module with membranes of varying selectivity. For the highly retentive membranes the results were very promising: TDS was lowered from 531 to 20 ppm, ABS from 3.0 to 0.1 ppm, COD from 38.8 to less than 1 ppm. Water flux was 2.5 gfd initially at 200 psi and decreased to 2 gfd over a period of nine weeks. Less selective membranes showed much larger decreases in flux because of fouling.

Azusa, Arizona, (14) used a laboratory scale wet up with a membrane area of one ft^2 and a closed loop water circulation system to enable high water recoveries. The membrane flux nominally varied from 10 to 60 gfd, and pressures of 750 and 1500 psi were utilized. The significant aspect of this test was the combination of high water recoveries with good removal. TDS was lowered from 550 to 15 ppm, ABS from 4.5 to .1 ppm and COD from 95 to 2 ppm. All the important nutrients (NH_4^+, NO_3^-, $PO_4^=$) were reduced to undetectable levels. Problems of flux decline with time due to compaction and membrane coating were encountered.

Bergen County, New Jersey (45), was the site of a 1400 gpd pilot plant. A spiral-wound module with a loop configuration allowing high circulation rates was used. Water recoveries of 50 per cent were maintained over the test period of one week. Only highly selective membranes were used. The product quality was very good. The rejection of all but nitrogen compounds was 90 per cent or greater. The following rejections were reported: TDS 96%, nitrates 70%, ammonia 90%, and BOD reduction from ranges of 8-26 to 1 ppm. ABS, odor and turbidity were practically eliminated. Flux was maintained constant at 8 gfd since the membranes had previously been used for a period of one week, which is normally adequate to stabilize the flux rate.

Unfortunately, little research has been done on the removal of organics similar to chlorinated hydrocarbon pesticides. Specific tests have been conducted on phenol and ABS. Phenol (46) has shown a strong tendency to penetrate cellulose acetate membranes. This is thought to be caused by high solubility of phenol in the membrane, and is significant because Lindane, the chlorinated hydrocarbon used in the research study reported herein, resembles phenol closely in size, shape, and composition. ABS, which is similar to Lindane in molecular weight, has been shown by a number of researchers to be easily removed by reverse osmosis membranes with high retentivity (14, 44, 45).

Finally, the basic question facing any practical system is its economy. Cost estimates for a 10 MGD reverse osmosis plant range from $0.25 to $1.00/1,000 gallons (26). These estimates depend on a number of factors as follows: flux is presumed to be 20 to 30 gfd; membrane life must be long or replacement must be inexpensive; pretreatment is necessary to prevent bacterial slimes from clogging the membrane; recovery to waste ratio is maintained high with minimum volume of raffinate; membrane costs are reasonable; and membrane demand is high enough to warrant mass production.

Although the membrane process of reverse osmosis has shown great promise, there is little knowledge of its capability of removing potentially harmful trace contaminants, and in fact, it may increase the problem in this area due to enrichment of permeate. This research was conducted to provide information relating to these unknowns.

3. THEORETICAL CONSIDERATIONS

A great deal of research has gone into developing mathematical models to predict the behavior of various solutes in reverse osmosis systems. Ideally it would be advantageous to have a formula which would relate a given solute, an initial concentration, a working pressure and a particular membrane to a final recovery ratio, a specific flux rate, and a calculated solute rejection efficiency. Elata (47) discussed a series of tests and equations which have been developed for this purpose.

To date the literature only contains information on salt and phenol relative to this type of calculation. Riley, et al (32) used coefficients derived in this manner in the solution-diffusion mathematical model to arrive at the theoretical salt rejections of brine utilizing an ultrathin cellulose acetate membrane.

Using the solution-diffusion equations (48) for salt and water fluxes:

$$F_s = D_s K \left(\frac{\Delta\rho_s}{\Delta X}\right) \qquad (14)$$

F_s = salt flux (g/cm^2-sec)

D_s = diffusion coefficient for salt in membrane (cm^2/sec)

K = distribution coefficient for salt (g/cm^3 membrane per g/cm^3 solution)

$\Delta\rho_s$ = salt concentration difference in the two solutions on both sides of the membrane (g/cm^3)

ΔX = distance perpendicular to the membrane (cm)

$$\text{Also,}\quad F_w = \frac{D_w C_w \overline{V}_w}{RT} \left(\frac{\Delta P - \Delta\pi}{\Delta X}\right) \cong A(\Delta P - \Delta\pi) \qquad (10\text{-}11)$$

F_w = water flux (g/cm^2-sec)

D_w = diffusion coefficient for water in the membrane (g/cm^3)

$\overline{V}_w$ = partial molar volume of water in the external phase (18 g/g-mole)

ΔP = pressure difference across the membrane (atm)

$\Delta\pi$ = osmotic pressure difference across the membrane (atm)

The salt rejection, S, is a function of solute and solvent fluxes:

$$S = \frac{\rho'_s - \rho''_s}{\rho'_s} \qquad (29)$$

$'$ = high pressure side of the membrane

$''$ = low pressure side of the membrane

The theoretical salt rejection can be calculated from the following equations:

$$S = 1 - \frac{J_s \rho''_w}{J_w \rho'_s} = \left[1 + \frac{D_s K R T \rho''_w}{D_w C_w \overline{V}_w (\Delta P - \Delta\pi)}\right] \qquad (30)$$

ρ_w = concentration of water outside of the membrane

Assuming:

temperature = 25°C = 298.15°K

concentration = 1% NaCl

composition = 39.8% - acetyl cellulose acetate

pressure = 500 psi (34 atm)

Known:

$D_w C_w$ = 2.6×10^{-7} g/cm-sec

$D_s K$ = 3.2×10^{-11} cm^2/sec

R = 82.0567 atm-cm^3/g mole-°K

ρ''_w = 1 g/cm^3

$\overline{V}_w$ = 18 g/g-mole

$\Delta\pi$ = 6.8 atm

$$S = [1 + \frac{(3.2 \times 10^{-11} cm^2/sec)(82.06 \frac{atm\ cm^3}{g\ mole°K})(298.15°K)(1g/cm^3)}{(2.6 \times 10^{-7}\ g/cm\text{-}sec)(18\ cm^3/g\text{-}mole)(34-6.8\ atm)}]$$

$S = 99.4\%$

The above calculated rejection very closely agrees with the results given by Merten (34) of 99.37%.

Lonsdale, et al (46) utilized the solution diffusion equation to analyze the theoretical phenol rejection. Again, the same flux equations were utilized. The standard rejection equation:

$$S = \frac{\rho'_s - \rho''_s}{\rho'_s} \qquad (29)$$

was defined as follows:

$$\frac{\rho'_s}{\rho''_s} = \frac{D_w \overline{V}_w K_w \Delta P + D_s K_s RT}{D_s K_s (RT + \overline{V}_s \Delta P)}$$

Given:

$\overline{V}_s$ = 90 cm^3/g-mole

D_wC_w = 2.1 x 10^{-7} g/cm-sec

K_w = $C_w/\rho_w \doteq C_w$

D_sK_s = 3.9 x 10^{-8} cm^2/sec

ΔP = 34 atm

T = 298.15 °K

$\overline{V}_w$ = 18 cm^3/g-mole

R = 82.0567 atm-cm^3/g-mole °K

$$\frac{\rho'}{\rho''_s} = \left[\frac{(2.8\text{x}10^{-7}\text{g/cm-sec})(18\frac{\text{cm}^3}{\text{g-mole}})(34\text{atm})+(3.9\text{x}10^{-8}\frac{\text{cm}^2}{\text{sec}})(82.06\frac{\text{atm-cm}^3}{\text{g mole}^{\circ}\text{K}})(298.15^{\circ}\text{K})}{(3.9\text{x}10^{-8}\text{cm}^2/\text{sec})[(82.06\frac{\text{atm-cm}^2}{\text{g-mole}^{\circ}\text{K}})(298.15^{\circ}\text{K})+(90\text{cm}^3/\text{g mole})(34\text{ atm})]}\right]$$

$$\frac{\rho'}{\rho''_s} = 1.01$$

$$S = .99\%$$

The derivation as reported by Lonsdale (46) had been corrected for 30°C, and resulted in a negative rejection of -1%. The actual results obtained by using a modified membrane at 34 atm pressure were -10.8% for two tests.

A frictional model was used by Merten, et al (34, 49) to predict the phenol rejection. They presented the following curve of calculated results and Table of related experimental results.

TABLE 3

REVERSE OSMOSIS RESULTS FOR PHENOL AT T = 30°C (34)

Applied Pressure (atm)	Membrane	Solute Rejection %
34	modified	-10.8, -10.8
68	modified	-17.4, -20.2
68	normal	-10.4, +1.3
102	modified	-20.3, -22.9
102	normal	(-27.1, -16.9, -13.9, -10.7, -25.7)

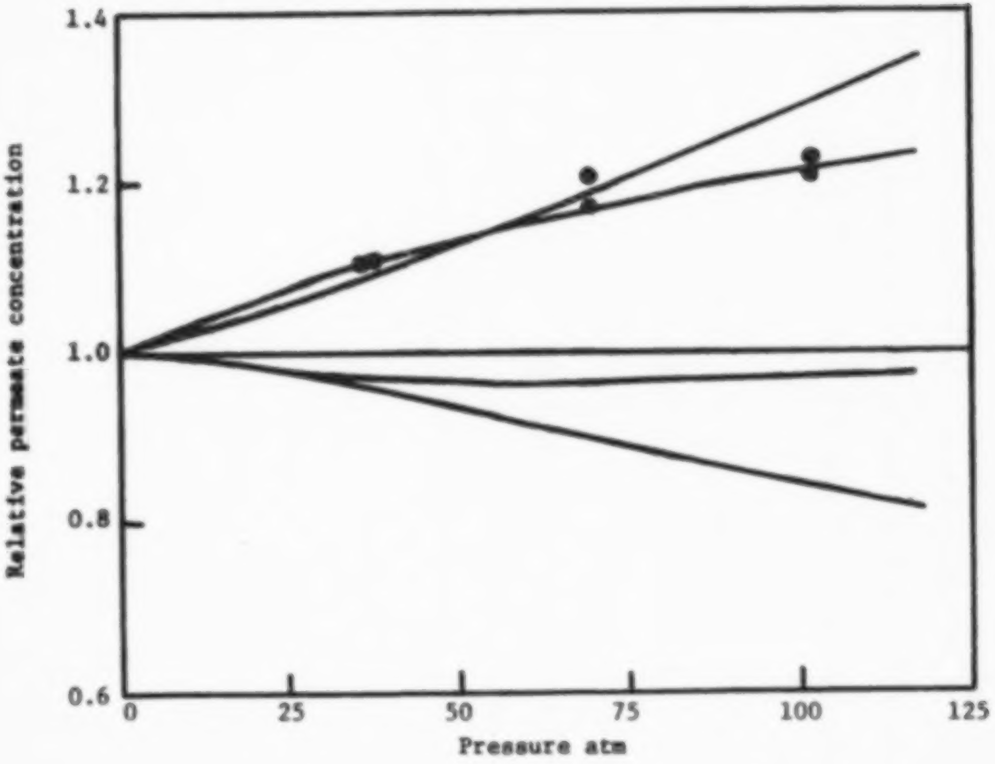

Fig. 8 CALCULATED PHENOL CURVES USING FRICTIONAL MODEL -- THE POINTS BEING ACTUAL RESULTS (34)

Another compound of interest in this research is Alkyl Benzene Sulphonate (ABS). A number of sources have given the per cent rejection of ABS in a cellulose acetate membrane. In the Azusa test (14) on wastewater using a laboratory scale reverse osmosis system, ABS was reduced from 4.5 to 0.1 ppm at pressures of 750 and 1500 psi. The Pomona test (44) utilized a much lower pressure of 200 psi, and with the most selective membrane reduced ABS from 3.0 to less than 0.1 ppm.

The membrane utilized in the research reported herein was Abcor HFA-100 modified cellulose acetate. It was utilized in a flat plate configuration with a calculated velocity of flow of 28.2 cm/sec over a surface area of 46 cm^2. It was felt that this velocity was adequate, considering the low reservoir concentration, to prevent any problems with concentration polarization especially in the case of ABS.

TABLE 4

TYPICAL PERFORMANCE OF ABCOR TYPE HFA-100 MEMBRANE (50)

Solute Type	Solute Weight %	Operating Pressure psig	Flux Rate gal/day/ft^2	Solute Retention Mol. Wt.	Solute Retention % Retention
Water	100	500	45	---	---
NaCl	0.5	500	40	58	35
Sucrose	3.0	500	40	342	80
Dextran Yellow	0.02	500	40	~20,000	>99

The foregoing data indicated that the membrane was not very tight in that it would not retain a high percentage of NaCl at 500 psi. The actual NaCl retention was 35% at 500 psi and .5% NaCl feed solution while the theoretical value for these parameters is 99.43% as derived from Eq. 30 by Lonsdale, et al (48).

Utilizing this information, a comparison between actual and theoretical retentions can be made for the compounds tested: lindane, pentachlorophenol and ABS, as well as for compounds reported in the literature, such as ABS, phenol, and NaCl. This comparison can be made on the basis of size, structure, weight, and solubility.

Utilizing data provided in the Handbook of Physics and Chemistry (51) the approximate sizes of the compounds of interest were calculated to be:

TABLE 5

SIZES OF COMPOUNDS STUDIED

Phenol = 4.96 Å and Mol. wt. 94 C_6H_5OH

Lindane = 6.19 Å and Mol. wt. 291 $C_6H_6Cl_6$

Pentachlorophenol = 6.19 or 5.57 Å and Mol. wt. 272.5 $C_6H_5Cl_5OH$

ABS = 16.9 Å and Mol. wt. 348.5 $C_{12}H_{25}C_6H_4SO_3Na$

On the basis of size, shape and weight the high retention of ABS in contrast to negative retention of phenol is understandable. The high solubility of phenol in the membrane was considered an important reason for its high negative retentivity (K for phenol was 42) (35, 46).

No data exists on the solubility of ABS in the cellulose acetate so that retention cannot be compared on this point. In addition, no data is available on the solubility of pentachlorophenol or lindane in cellulose acetate. Thus, the retentivity of lindane and pentachlorophenol can only be predicted on the basis of size, shape, and molecular weight. Based on structure, size, and composition, lindane and pentachlorophenol would be expected to follow a course similar to phenol. Based on molecular weight, these two chlorinated hydrocarbons would be expected to be similar to ABS in retentivity.

Solubility in water of lindane is approximately 10 ppm (52, 53), phenol is 66,600 (54), and pentachlorophenol is 80 ppm (54). These solubilities in water indicate that pentachlorophenol and lindane are not similar to phenol. If the aversion of lindane for water is balanced by a high solubility in cellulose acetate, then lindane could possibly behave in a manner similar to phenol. The same relationship could apply to pentachlorophenol.

4. EXPERIMENTAL EQUIPMENT AND PROCEDURES

The reverse osmosis apparatus utilized was a laboratory scale, flat-plate system. A schematic diagram of this system is illustrated in Fig. 9. Contaminated water was pumped from the reservoir through a flowrator, and the reverse osmosis cell, and then was recycled back to the reservoir. A tee connection ahead of the flowrator provided a by-pass, which allowed controlled flow through the cell. In the experiments, a flow of 0.54 gpm of feed water was maintained, which provided a velocity of .925 ft/sec over the membrane. Control of the flow was achieved by manipulation of two gate valves: one just prior to the flowrator and a second in the by-pass line. System pressure was maintained by nitrogen gas applied to the reservoir. The pressure at the membrane was a combination of pressure applied at the reservoir, pump pressure, and friction losses. The pressure at the membrane was determined by a bourdon tube pressure gage located approximately two feet before the membrane cell on the feed line. It was felt that pipe friction losses to the cell would be small enough to ignore over this distance.

The reverse osmosis cell, Fig. 4, was a machined plastic block especially designed for reverse osmosis studies and provided by Dorr-Oliver, Inc. The membrane was supported on a porous backing material overlying a grid of collection channels machined in the pure water side of the cell. The flow over the membrane was maintained at a much higher rate than the water flux through the membrane. Thus, hydraulic

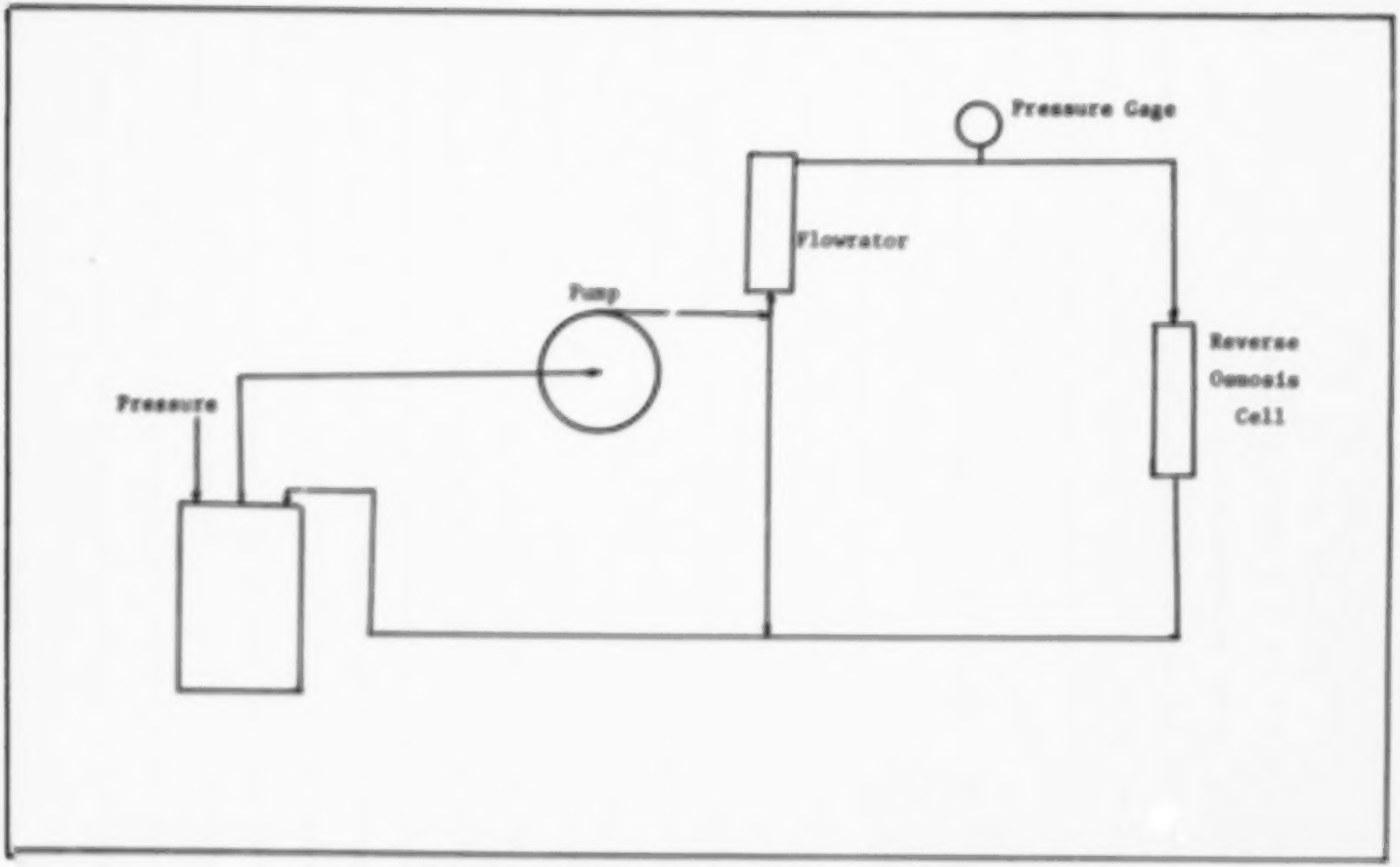
Pressure Gage
Flowrator
Pump
Pressure
Reverse
Osmosis
Cell

Fig. 9 SCHEMATIC DIAGRAM OF LABORATORY REVERSE OSMOSIS SYSTEM

scrubbing was used to prevent a development of concentration polarization. In any one series of tests, the amount of sample water extracted through the membrane was a small fraction of the reservoir volume (reservoir volume = 3 gallons). This small sample to reservoir ratio prevented any significant change in reservoir concentration due to solute rejection by the membrane. Water and solute which passed over the membrane without permeation returned to the reservoir.

The membrane utilized in this study was provided by Abcor, Inc., of Cambridge, Massachusetts. This membrane is the tightest of a series of membranes manufactured by this company. A relatively high-retention membrane was desirable because of the low molecular weights of the organic contaminants investigated. Typical performance data of the HFA-100 membrane used as given by the manufacturer (50) is presented in Table 4.

Operating pressures of 30, 40, and 50 psi were selected as practical range for economical reverse osmosis treatment of contaminated waters. A primary consideration in the practicality of this range is the ease in obtaining, operating, and maintaining equipment designed for this pressure range as compared with common operating pressures for desalination of 750 to 1500 psi. Since these pressures were lower than those on which performance was reported by the manufacturer of the membrane, initial flux and temperature data were collected on a system containing distilled water only.

This series of pure water tests established the flux rates at different pressures and temperatures. It was continued as a practice throughout the experiments to monitor temperature, pressure, pH, flux, and feed water circulation rates.

4.1 STUDIES ON REMOVAL OF ABS

Seven studies were conducted on ABS. Three were conducted at 50 psi with concentrations of 0.5, 2.0, and 4.0 ppm, and four were carried out at 30 and 40 psi with concentrations of 2.0 and 4.0 ppm of ABS. Initial and final temperatures of the system and water flux rates of the permeate were recorded. The per cent solute retention was determined by collecting measured volumes of permeate and determining quantities of solute present. Since the system concentration was known, per cent solute retained and passed could be derived.

The analytical method of measuring ABS was according to Standard Methods for the Examination of Water and Wastewater (55). The methylene blue method selected was listed as tentative in the text, but it is the preferred method of the two listed. In principal, the method depends on the formation of a blue-colored salt when methylene blue reacts with anionic surfactants, which include not only ABS, but also alkyl sulfates. The salt is highly soluble in chloroform, and the intensity of color is proportional to the concentration. The intensity of color was measured by spectrophotometric readings of the solvent extraction at a wavelength of 652 mμ. The method can be utilized for concentrations of 0.025 to 100 mg/l as ABS.

Interference in the methylene blue ABS test can come from both organic and inorganic materials. Positive interference may be caused by organic sulphates, sulfonates, carboxylates, phosphates, phenols, inorganic cyanates, chlorides, nitrates, and thiocyanates. Negative results could be due to organic materials, especially amines, which compete with the methylene blue in the reaction. Positive results are the more common of the two. In the study reported herein, interferences should have been negligible, since only distilled water with pure compound ABS was utilized.

The procedure of measurement was as follows:

(1) Preparation of calibration curves

A series of ten separatory funnels with 0.00, 1.00, 3.00, 5.00, 7.00, 9.00, 11.00, 13.00, 15.00, and 20.00 ml of standard ABS solution was prepared using a standard solution having a concentration of 1.00 mg/l ABS. Sufficient water was added to each separatory funnel to make a total volume of 100 ml. The samples were extracted and measured as described in Section 3 below. A calibration curve of mg ABS versus per cent transmittance was then plotted.

(2) Volume required

The volume of the sample tested depended on the expected ABS concentration, according to the following:

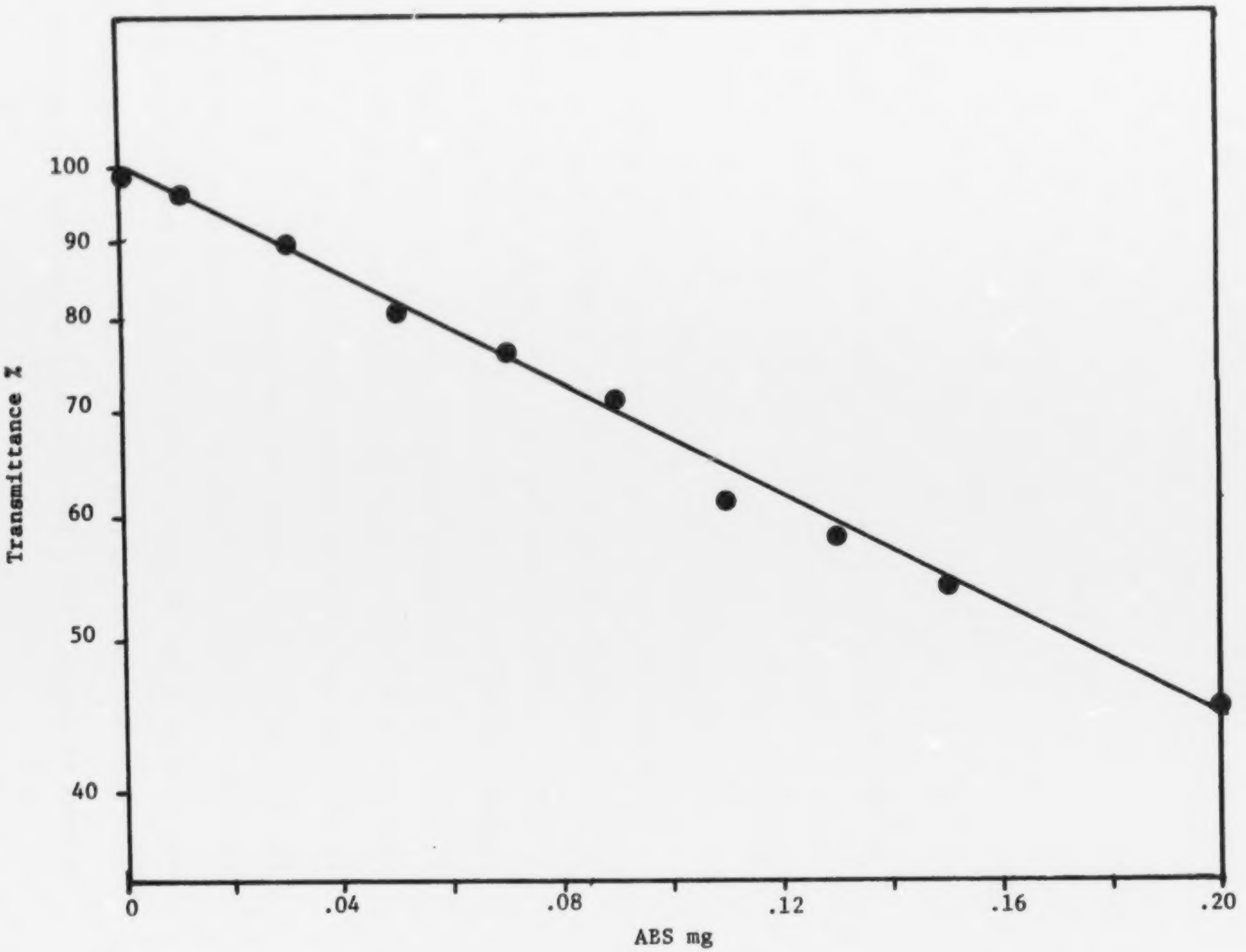

Fig. 10 ABS CALIBRATION CURVE

Expected ABS Concentration, mg/l	Sample, ml
0.025 - 0.080	400
0.080 - 0.40	250
0.40 - 2.0	100
2. 10.	20.0
10. 100.	2.00

If the sample indicated was smaller than 100 ml, it was diluted to 100 ml. If the sample indicated was larger than 100 ml, the entire sample was used.

(3) Extraction and color development

The solution was first made alkaline by adding 1N NaOH, and it was then acidified with 1N H_2SO_4 using phenophthalein as the indicator. 10 ml of chloroform and 25 ml of a stock methylene blue reagent was then added, and the separatory funnel was swirled in a circular motion for approximately 30 seconds. The two phases were then allowed to separate with the chloroform settling to the bottom. It was drawn off into a second separatory funnel and the extraction procedure on the water sample was repeated twice more. All the chloroform extracts were collected in the second separatory funnel, and 50 ml of a wash solution (acidic solution of $NaH_2PO_4 \cdot H_2O$) was added. The separatory funnel was then swirled vigorously for 30 seconds and allowed to settle. The chloroform layer was drained into a 100 ml volumetric flask through a layer of glass wool. The wash procedure was repeated twice more with 10 ml portions of wash solution. After the washing step, the glass wool and funnel were rinsed with chloroform, and all the chloroform was collected in a volumetric flask. It was diluted to the 100 ml mark for spectrophotometric measurement.

(4) Measurement and calculation

Using a Spectronic 20 spectrophotometer, the transmittance of the colored solution was measured with a light wavelength of 652 mμ, against a blank of chloroform.

The concentration of ABS was calculated as:

$$\text{mg/l total apparent ABS} = \frac{\text{mg ABS} \times 1{,}000}{\text{ml sample}} \qquad (32)$$

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4.2 STUDIES ON REMOVAL OF LINDANE

Lindane, a chloronated hydrocarbon pesticide, was investigated for per cent retention under conditions similar to the ABS reverse osmosis studies. Fifteen studies were conducted utilizing pressures of 30, 40, and 50 psi. The concentrations of the tests ranged from approximately .00739 to 1.93 ppm.

Stock solutions for the reservoir were prepared initially by heating suspensions of water and lindane in three-liter flasks. After the lindane crystals appeared to have dissolved, the solutions were stirred overnight in a 20-liter glass carboy. A second stock solution was prepared by stirring 15 liters of distilled water and lindane crystals for approximately 24 hours. Both stock solutions contained some undissolved lindane crystals.

The first stock solution was added to the reservoir for two series of tests. In the first, 25% of the system volume was comprised of stock solution with the remainder being distilled water. In the second series of tests, 50% of the system volume consisted of stock solution. A third series of tests utilized the second unheated stock solution without dilution. These stock solutions were added to the reservoir without filtration of the suspended matter, but a siphon was used to transfer the solution from the carboy, so that no lindane crystals would be transferred. Tests were run at 30, 40, and 50 psi. Sample sizes collected were 100 ml and redistilled petroleum ether was used as the solvent for extractions. Reservoir samples for the 25 and 100 per cent solutions and both stocks were extracted so that per cent rejection could be determined.

A final sequence of tests was run with an effort made to maintain a higher and more constant reservoir concentration of lindane. In this series only one stock solution was prepared. Five three-liter erlenmeyer flasks were charged with a sufficient amount of recrystalized lindane to make a 10 mg/l solution in distilled water. Each flask was heated to a temperature close to boiling and stirred overnight. The reverse osmosis system volume was charged with this undiluted stock solution. Since even recrystalization failed to make lindane soluble to 10 mg/l, the solubility given by Negerbon (53), the stock solution was filtered through glass wool before addition to the reservoir.

The reservoir concentration was sampled after circulating the reservoir water for 15 minutes, which was an adequate time to insure a uniform solution. Two series of reverse osmosis tests were run over a three-day period without changing reservoir solution. In each series of tests, 100 ml samples were collected after permeation through the membrane. Reservoir samples also of 100 ml volume were collected prior to and after each series of runs at the three pressures utilized.

The solvent utilized in the first sequence was petroleum ether, while redistilled benzene was used in the final sequence of tests. The extraction procedures were essentially the same in all the lindane tests. The collected samples were placed in a separatory funnel and the volumetric flask washed with distilled water. The solvent was then added in ratio of 1 part solvent to 5 parts sample volume. This varied according to the amount of wash water used in the volumetric flasks. The mixture in the separatory funnel was then agitated for approximately 30 seconds. After settling the water was drained off to a second separatory funnel for a second extraction. The extraction was performed three times. The funnels were rinsed with solvent after each use and the solvent, which then contained trace amounts of water, was filtered through anhydrous sodium sulphate and glass wool. The sodium sulphate layer served to remove any trapped water from the solvent and the glass wool supported the sodium sulphate. This filter was rinsed with solvent before and after use. All glassware was given a final rinse of solvent before use, since detergent would be a major source of interference.

Following collection, the solvent was evaporated to dryness in the hood. Once dry the beaker was covered to prevent loss of lindane by volatilization. The collected lindane was then rinsed with solvent into volumetric flasks of 5 or 10 ml capacity. In this way the collected sample was effectively concentrated 10 to 20 times.

An electron capture gas chromatograph was used to analyze the solvent for lindane (56). The electron capture detector is the most sensitive detector used in pesticide analysis. It is capable of detecting as little as 1×10^{-12}g of material depending on the sophistication of the remainder of the system.

In principal, the detector uses a radioactive source to emit electrons (Fig. 11). These electrons accumulate in the plasma adjacent to the cathode (56). When a pulsed potential is applied, a current flows between the cathode and the anode. If the electron capturing components are introduced into the plasma, one or more electrons are lost. The loss of electrons causes a corresponding decrease in cell current which is amplified and recorded to produce a peak on the chart. Chlorinated hydrocarbons have great affinity for electrons, so they produce a very strong chromatographic reaction.

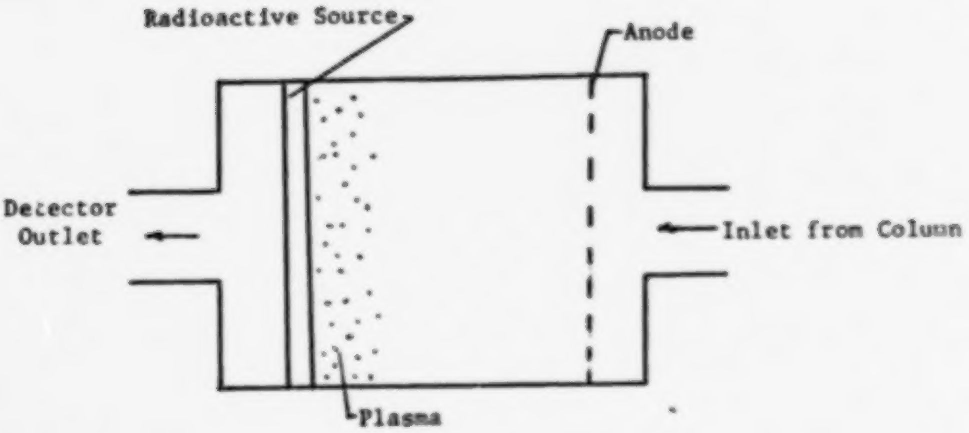
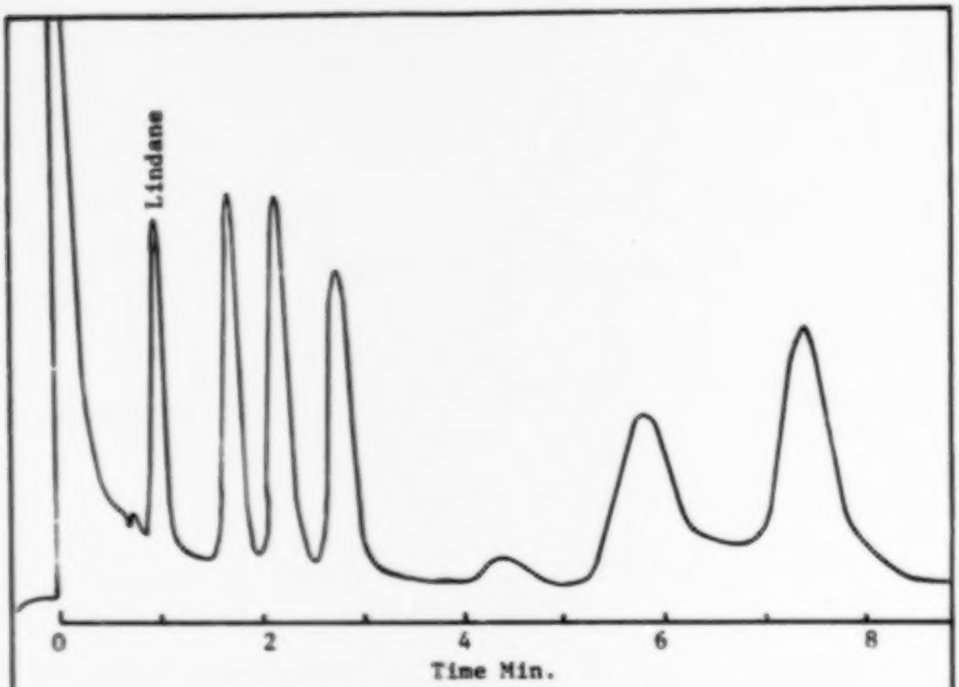


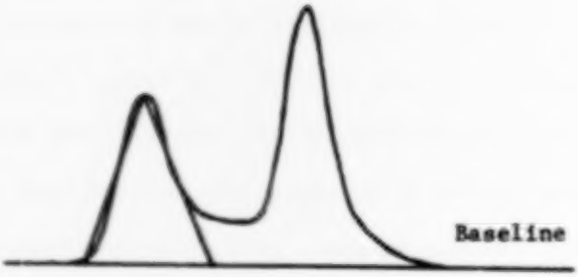
Fig. 11 GAS CHROMATOGRAPH DETECTOR (56)

Separation of various components of sample before reaching the gas chromatography detector is achieved by use of a column which permits different components to pass at different rates. Generally, the lower the boiling point and the smaller the molecule, the lower the retention time in the column (57). Thus, the solvent used in the analysis required several seconds to pass, while lindane required approximately one minute.

The concentration of the pesticide in a solvent is determined by injecting a measured amount of solution into the gas chromatograph. Injection was accomplished using a 10 μl syringe and utilizing volumes



TYPICAL PESTICIDE GAS CHROMATOGRAPH PEAKS



TRIANGULATION METHOD FOR AREA DETERMINATION

Fig. 12 GAS CHROMATOGRAPH PEAKS AND AREA DETERMINATION

from .6 μl to 6.0 μl. The detection and measurement of the pesticide resulted in a peak which was generally quite sharp and could be measured by triangulation to determine its area. By comparing the area of this sample peak with the peaks recorded for control samples, the concentration of the sample could be derived. Since the response of the detector doesn't always follow a linear relationship to the amount of sample injected, the samples were adjusted in volume to yield peak areas similar to the areas of the sample peaks.

4.3 STUDIES ON REMOVAL OF PENTACHLOROPHENOL

Tests were run on pentachlorophenol because of its structural relationship to lindane as well as published results of normal phenol permeation through reverse osmosis membranes. Thus, it was anticipated that the degree of rejection of the three compounds would correspond with their similarity in structure and size.

A stock solution of pentachlorophenol was prepared by stirring the compound in distilled water for approximately 24 hours at a pH of 9. The pH was adjusted using NaOH. The stock solution was made at a concentration of approximately 20 mg/l so that when the 6 liters of stock solution were added to the reservoir a concentration of 10 mg/l would be achieved in the 12.5 liter system. In actuality, a solution of 20 mg/l was not achieved. The stock was readjusted to a pH of 6 before addition to the reservoir since this was the initial distilled water pH. To insure the presence of only soluble pentachlorophenol in the reservoir, the stock was filtered through glass wool.

Solvent extraction was achieved using redistilled benzene and the same procedure as was outlined for lindane. The evaporation and concentration procedure were also identical, except 10 ml volumetric flasks were used for all the concentrated samples.

Analysis of the pentachlorophenol was first attempted using the electron capture gas chromatograph. However, it was found that the sensitivity of the instrument was very low and column separation was poor. The compound was apparently leaking through the column very slowly as was indicated by a slow upward drift in base line. Subsequently, a Perkin Elmer model ultraviolet spectrophotometer was utilized at a wavelength of 303 mμ.

The ultraviolet spectrophotometer operates by splitting a beam of light into two beams. One beam passes through a reference sample filled with solvent alone. The second beam passes through the sample. Because transmittance is unbalanced, a motor will move an attenuator wedge until the light reaching the detector from both beams is equal. The motor which activates the attenuator wedge also controls the recorder pen. The ultraviolet range of scan for the instrument is from 190 to 390 millimicrons. This entire spectrum will be scanned by the instrument and peaks recorded at the wavelengths at which the compound absorbs radiant energy. The area under the recorded peaks or peak height at a certain wavelength can be used to measure concentration (58). A reference set of curves was established for 5 to 120 ppm of pentachlorophenol. Fig. 13 shows peak height at 303 mμ vs. concentration.

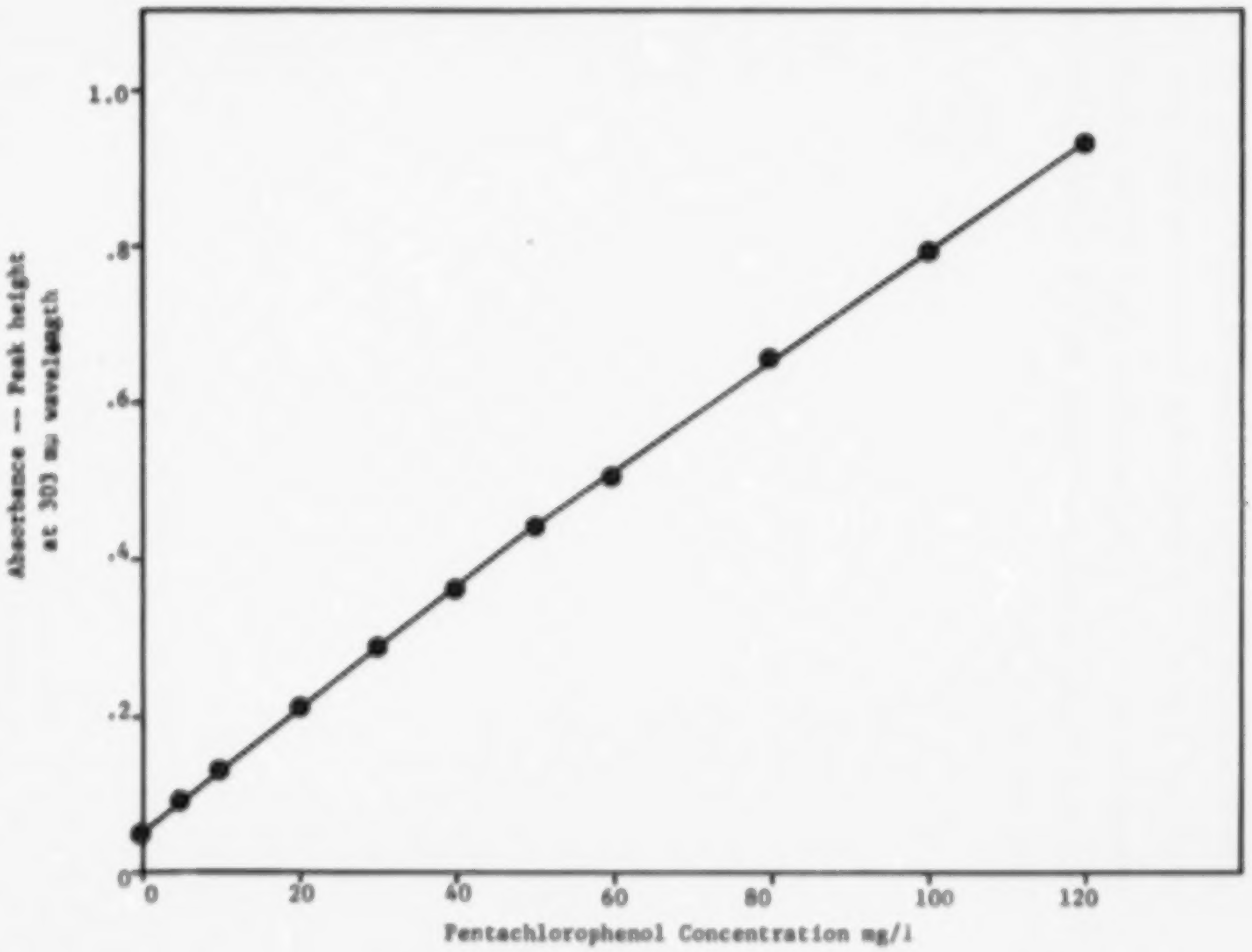


Fig. 13 PENTACHLOROPHENOL CALIBRATION CURVE

It was found that the teflon sealing compound used in the connections of the reverse osmosis caused an interference in the UV at 285 millimicrons. The interference peak was broad and high. Although the teflon was quite insoluble in water, it was sufficiently soluble in benzene so that interference resulted from this source by extraction of samples.

5. EXPERIMENTAL RESULTS AND DISCUSSION

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5.1 PERMEATE FLUX RATES

Initial studies were made upon the Abcor, Inc., HFA-100 membranes to establish the reltionship between operating pressures, temperatures, and the permeate flux rates which would be obtained in the pressure range of 30 to 50 psi utilized in the studies. This preliminary work was necessary because the membranes were actually designed for operating pressures of 500 psi, and very few membranes designed for 30 to 50 psi are available at the present time on the market.

The results of the base line studies on pressure, temperature, and permeate flux interdependence are shown in Table 6 and Fig. 14. It can be seen that even though the membrane was developed for operation under 500 psi pressure, a significant flux rate was obtained at 30 to 50 psi in these studies. An approximately straight line relationship was exhibited between pressure and flux rates. For example, Table 4 indicates that the flux at 500 psi would be 45 gfd, while the rates of permeation in these studies, although variable with temperature, were in the range of 3.46 to 4.31 gfd at 50 psi.

5.1.1 EFFECTS OF PRESSURE

It can be seen that the permeate flux rates varied significantly with pressure, which is in accordance with both solution-diffusion and pore flow equations. The experimental results indicated that sufficiently great flux rates were obtained under lower operating pressures to warrant

TABLE 6

COMPARISON OF WATER FLUX, TEMPERATURE, AND PRESSURE UTILIZING ABCOR HFA-100 MEMBRANE

Pressure-psi	Water Flux-Gal/day/ft^2	Temperature-°C
30	2.34	28.
	2.38	31.
	2.50	31.5
	2.56	31.5
	2.59	34.75
40	3.20	30.5
	3.38	33.75
	3.39	34.
	3.57	35.
50	3.46	24.
	3.79	28.5
	3.86	29.
	3.90	31.5
	4.02	32.0
	4.06	32.5
	4.31	35.

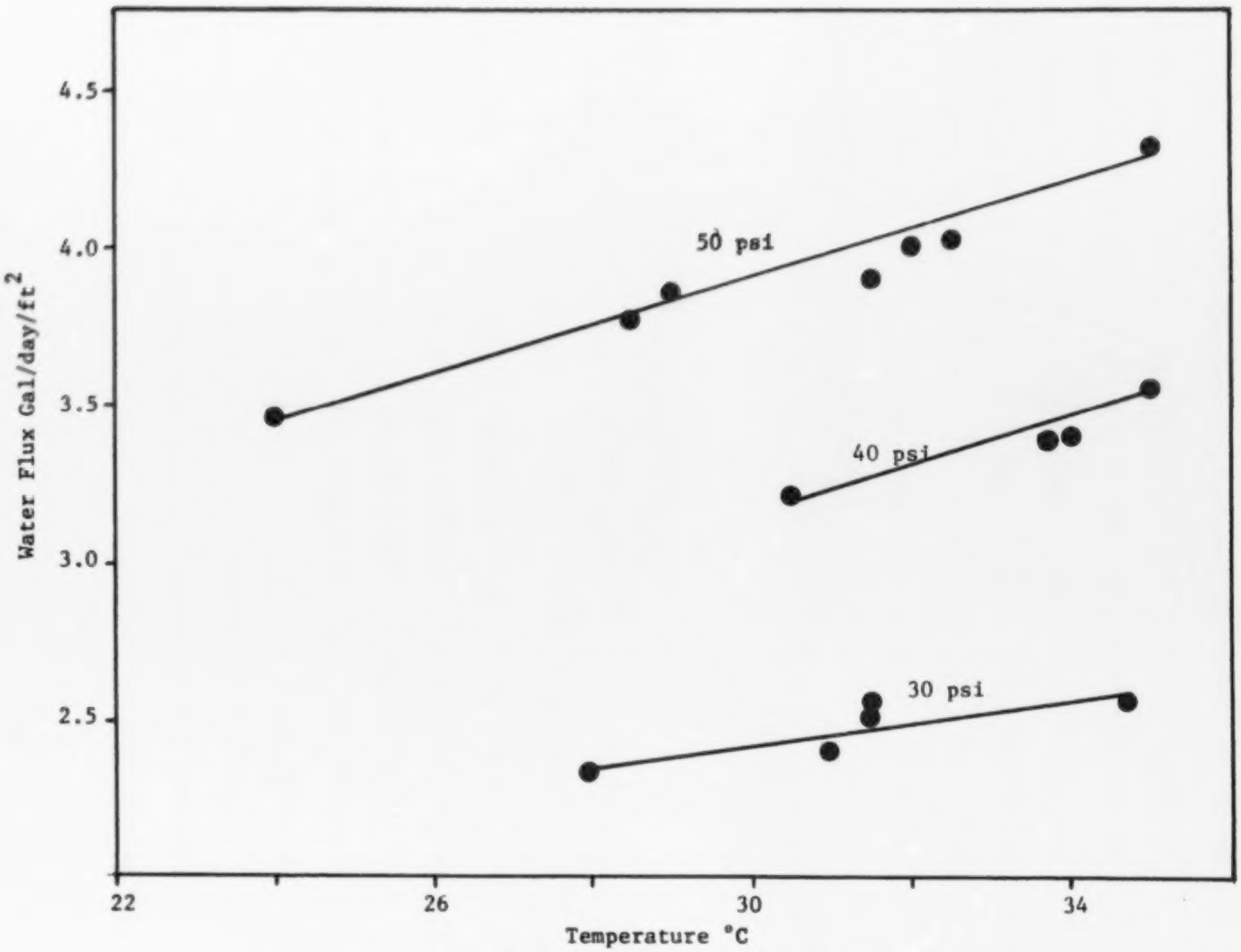

Fig. 14 WATER FLUX, TEMPERATURE, PRESSURE RELATIONSHIPS UTILIZING ABCOR HFA-100 MEMBRANE

continued study utilizing this membrane for removal of trace organic matter from water and wastewater. Membranes being developed by other firms exhibit flux rates of approximately 10 gal/day/ft^2 at the applied pressures, and although this rate is considerably higher than that obtained with the HFA-100 membrane, it is entirely possible that slight variations in processing of the membrane could allow its further development for higher flux densities at low pressures.

It can be seen from Table 6 and Fig. 14 that the effect of pressure on the flux rate followed approximately the reverse osmosis equation:

$$F_w = A(\Delta P_T - \Delta\pi) \qquad (10)$$

Where A is the permeability constant.

Since $\Delta\pi = 0$ in the absence of solute:

$$F_w = A\Delta P_T$$

As seen in Fig. 14, at a temperature of 34°C, the flux increased from 2.6 gal/day/ft^2 at 30 psi to 4.25 gal/day/ft^2 at 50 psi. According to the above equation, the permeate flux should theoretically have increased from 2.6 to 4.33 gal/day/ft^2 as the pressure increased from 30 to 50 psi.

A second set of data was taken at a later time. In this case the same membrane was used, but it had been previously exposed to air bubbles with a resulting partial drying of the membrane surface. The

TABLE 7

COMPARISON OF WATER FLUX, TEMPERATURE, AND PRESSURE UTILIZING MEMBRANE MODIFIED BY AIR EXPOSURE

Pressure psi	Water Flux gal/day/ft^2	Temperature °C
30	2.08	26.5
	2.03	28.5
	2.09	29.5
	2.16	31.5
	2.18	31.5
	2.22	31.75
40	2.79	30.
	2.97	32.
	3.02	33.
50	3.27	26.
	3.31	27.25
	3.25	27.75
	3.46	29.25
	3.52	31.25
	3.73	33.25
	3.72	34.
	3.81	34.25

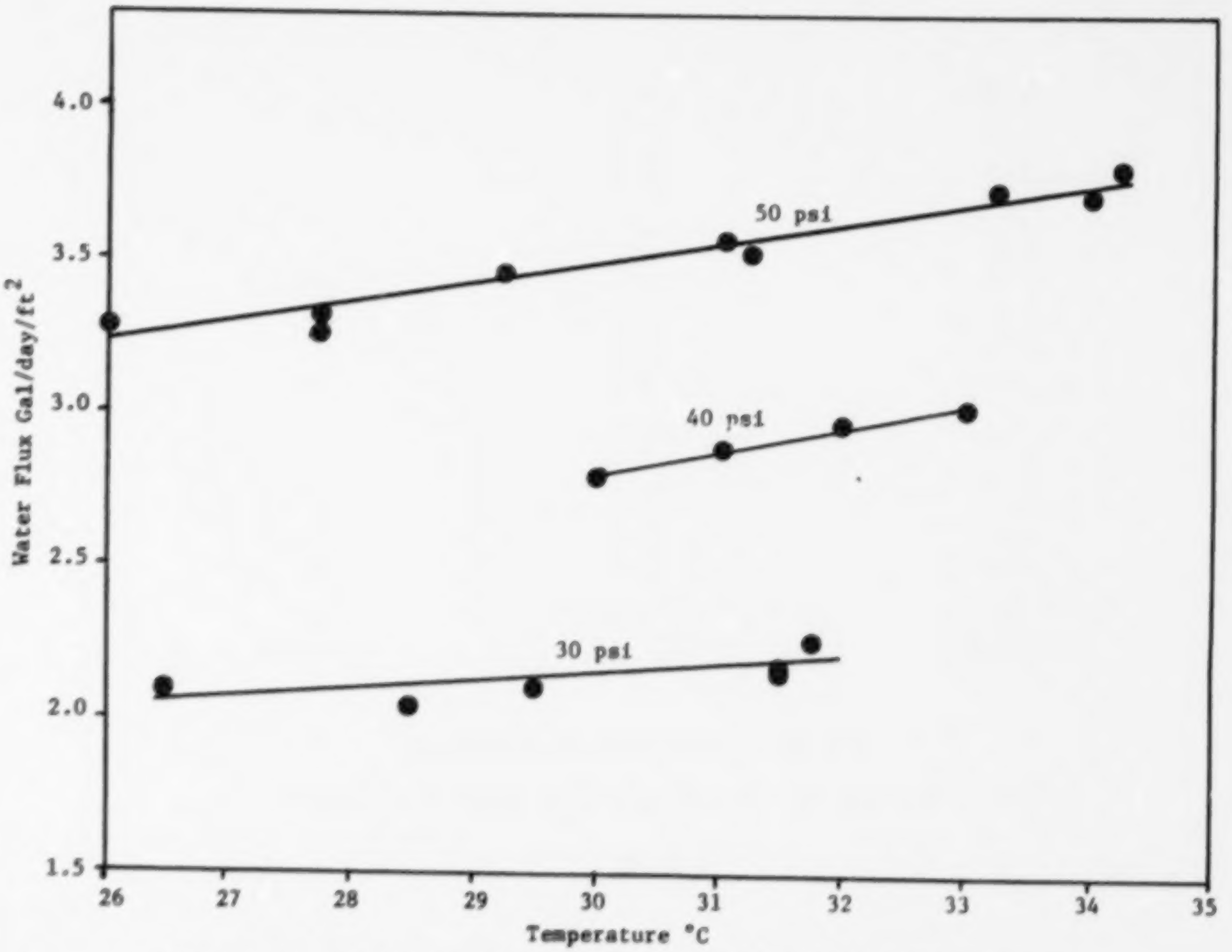

Fig. 15 WATER FLUX, TEMPERATURE, AND PRESSURE RELATIONSHIPS UTILIZING A MEMBRANE MODIFIED BY AIR EXPOSURE

resulting collapsing of membrane pores or changes in lattice structure was indicated by the slight difference in flux rates, as shown in Table 7 and Fig. 15. The second set of data resulted in slightly lower flux rates for the same pressures and temperatures, but the effects of both pressure and temperature were identical to those in the initial series of baseline tests.

5.1.2 EFFECTS OF TEMPERATURE

The baseline data indicated that there was a significant effect of temperature on the permeate flux rate. Lonsdale, et al (48) reported a similar temperature dependence in permeate flux studies. He noted a doubling of flux rates over a 33°C rise in temperature, while this research indicated a doubling of flux rate in approximately 50°C. Although a 2% increase in flux rate per degree C was slightly lower than the 3% increase per degree C reported by Lonsdale, et al (48), this difference may be due to differences in types of membranes, temperatures, and pressures under which the two research efforts were conducted. These research studies were conducted over a temperature range of 24 to 35°C, while the research reported by Lonsdale was conducted at 34 atmosphere pressure, or 500 psi, while the operating pressures in this research were between 30 and 50 psi.

5.2 STRUCTURAL CONFIGURATIONS OF COMPOUNDS STUDIED

The compounds separated from aqueous solution in this study were alkyl benzene sulphonate, lindane, and pentachlorophenol. These

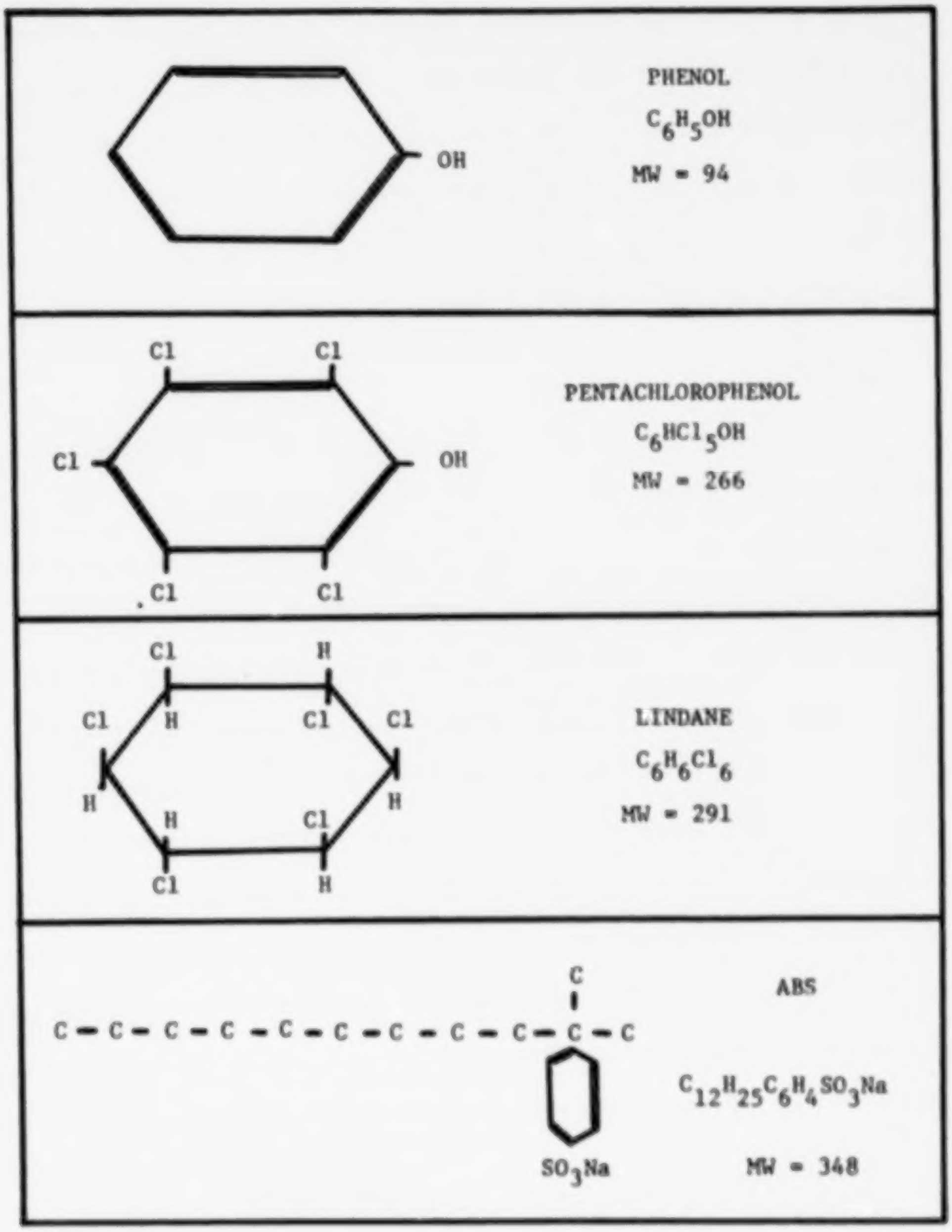
OH
PHENOL
C_6H_5OH
MW = 94
Cl
Cl
Cl
OH
Cl
Cl
PENTACHLOROPHENOL
C_6HCl_5OH
MW = 266
Cl
H
Cl
H
Cl
Cl
H
H
H
Cl
Cl
H
LINDANE
$C_6H_6Cl_6$
MW = 291
C
C – C – C – C – C – C – C – C – C – C – C
SO_3Na
ABS
$C_{12}H_{25}C_6H_4SO_3Na$
MW = 348

Fig. 16 MOLECULAR DIAGRAMS OF COMPOUND STUDIED

compounds, along with phenol for purposes of comparison, are illustrated in Fig. 16.

5.3 ALKYL BENZENE SULFONATE STUDIES

Alkyl Benzene Sulfonate was found to exhibit a number of characteristics suitable for its use in this study. It was readily soluble, easily removed from water samples by means of chloroform for subsequent analysis, and readily analyzed by spectrophotometric methods. The calibration curve for ABS vs per cent transmittance utilizing the spectrophotometer is given in Fig. 10.

Laboratory results obtained on rejection of ABS by reverse osmosis are presented in Table 8 and Fig. 17. ABS was found to be removed with considerable efficiency by reverse osmosis under the conditions of concentration and pressure employed. The per cent retention varied from 76 per cent at 50 psi in treating an 0.5 ppm ABS solution to 41 per cent at 30 psi using a 4 ppm solution.

It is seen that per cent retention decreased with increasing concentration and/or decreasing pressure. These results are in accordance with the solution-diffusion equations, which state that solute flux is concentration dependent and solvent flux is pressure dependent. Since the solute flux increases with concentration, it could be anticipated that the permeate at 4 ppm of ABS would contain a higher concentration of contaminants than the permeate at 0.5 ppm ABS concentration. Also, the permeate at 30 psi could be expected to contain a higher concentration of contaminants than the permeate at 50 psi since solvent

TABLE 8

ABS REMOVAL BY REVERSE OSMOSIS USING ANCOR HFA-100 MEMBRANE

Pressure	Concentration	Flux	Conc. in Permeate	% Solute Retention
psi	ppm	$gal/ft^2/day$	ppm	
30	2.0	2.56	1.03	48
	4.0	2.54	2.37	41
40	2.0	3.58	.68	66
	4.0	3.28	1.76	56
50	0.5	3.78	.104	79
	2.0	4.07	.615	69
	4.0	4.02	1.30	68

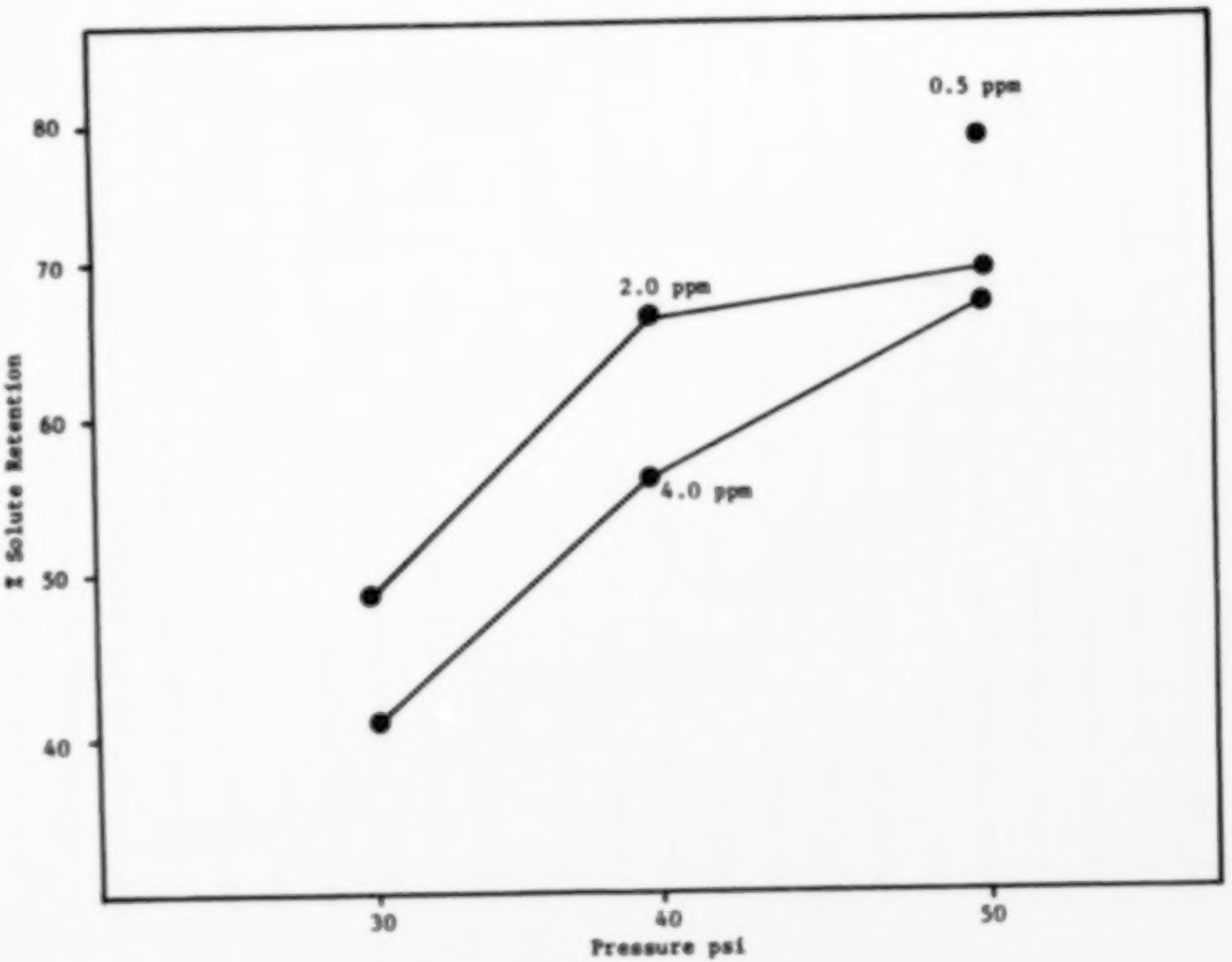

Fig. 17 REMOVAL OF ABS BY REVERSE OSMOSIS
USING HFA-100 ABCOR MEMBRANE

flux increases with pressure.

The viscous (pore) flow model would also apply to the observed results. The pore flow model gave the total volumetric flow including both solvent and solute, as being dependent on both pressure and concentration. This model allows for a coupling of solute and solvent flows. Examination of the results showed a reduction of total volumetric flow with a decrease in pressure and concentration. It is to be anticipated that either coupling of solute and solvent or imperfections may exist in the HFA-100 membrane. This is evident from the low actual rejection of 0.5% NaCl at 500 psi which was 35% (51) as opposed to the calculated theoretical rejection under these conditions of 99.46%. Thus, it may be that the viscous or frictional model is more appropriate to the HFA-100 membrane than the solution-diffusion model.

5.4 LINDANE STUDIES

Samples containing lindane were investigated at various initial lindane concentrations from 7.4 to 1,050 μg/l. The results of these studies, at pressures of 30 to 50 psi, are shown in Table 9. The right hand column of the table indicates the number of hours elapsed between initiation of the study and collection of the sample permeate.

Because of limitations caused by malfunctioning of the laboratory gas chromatograph and unavailability of a borrowed gas chromatograph for extended periods of time, the results obtained with lindane were necessarily very limited and should be considered as preliminary only.

TABLE 9

LINDANE RESULTS

Reservoir Concentration μg/l	Permeate Concentration μg/l	Operating Time per test hrs.
17.2	.632	2.84
	14.3	6.22
	41.3	10.51
34.4	29.2	2.75
	46.8	5.92
7.39	1.91	4.50
	2.60	7.70
1,930.	135.	4.83
	116.	8.16
136.*	237.	12.00
43.1	446.	5.12
	320.	8.67
7.6*	80.3	11.54

*Final reservoir concentration

An observation which appeared to be significant based upon the preliminary data was the increase in lindane concentration in the permeate samples as each experiment progressed. There appeared to be effective lindane rejection until the membrane became saturated with lindane, followed by bleeding through of lindane into the permeate from that point, to the degree where in some cases the permeate was even enriched in lindane over the lindane content in the bulk fluid.

In Table 9, the five initial bulk fluid concentrations are shown in the sequential order in which the experimental work was carried out. Beginning initially with a concentration of 17.2 μg/l, the permeate concentration at the end of 2.84 hours was 0.6 μg/l. After 6.2 hours the permeate contained 14 μg/l, and by the end of 10.51 hours, it had become enriched to 41 μg/l. When the bulk fluid concentration was increased to 34.4 μg/l, the initial sample taken after 2.75 hours indicated a permeate concentration of 29 μg/l. This increased to 46 μg/l after 5.92 hours. Similarly, in another experiment utilizing an initial concentration of 7.4 μg/l, the initial sample taken after 4.5 hours contained 1.9 μg/l of lindane in the permeate. This concentration increased to 2.6 μg/l after 7.70 hours.

It was decided at this point in the experiment to proceed to higher initial bulk flow concentrations of lindane. At initial concentrations of 1,930 μg/l, the lindane concentration of the permeate after 4.83 hours was 135 μg/l. The determination made after 8.16 hours was 116 μg/l, which increased to 237 μg/l after 12.00 hours. In a further study utilizing the same membrane, which apparently had become saturated with lindane, a very dilute sample of lindane in the bulk fluid resulted in decreasing concentrations of lindane in the permeate as the experiment progressed. Utilizing 43.1 μg/l initially, the permeate concentration ranged from 446 μg/l after 5.12 hours of operation, when much of the lindane on the surface of the membrane or saturated throughout the membrane had passed on into the permeate, to 320 μg/l after 8.67 hours and finally 80 μg/l after 11.54 hours of operation.

It is stressed that the above data is indeed preliminary in nature, but based upon an analysis of the data at hand, an initial observation can be made that the membrane utilized in these studies was not highly efficient in removing lindane from aqueous solution. A second observation is that the lindane apparently was rejected to a greater degree during the initial period of operation. The membrane apparently acted much like the media utilized in a chromatographic system, in that when the membrane's surface or the membrane itself became saturated with lindane, it would then allow bleeding through of the lindane into the permeate. This hypothesis is born out further by the final experimental results shown in Table 9. In this case a very dilute lindane solution, corresponding approximately to distilled water, was investigated using a membrane which had been previously exposed to high concentrations of lindane. The initial two samples taken after 5.12 and 8.67 hours of operation respectively, indicated practically no relationship between the extremely high concentrations of lindane in the permeate and the low concentration in the bulk fluid, except for the amount of lindane which may have been on or in the membrane when the experiment was initiated. After some 11.54 hours of operation, the permeate was still enriched in lindane, but at this point it was much more near to the lindane concentration in the bulk fluid.

The above data must be further validated before a complete understanding is reached regarding the effects of this membrane upon lindane rejection by reverse osmosis or ultrafiltration. At least three basic considerations require such validation of verification. First, the compound lindane is extremely hydrophobic and sparingly soluble in aqueous solution. Being sparingly soluble, it tends to adsorb readily upon all surfaces of containers in which it comes into contact. Its sorption to various surfaces is a function of the type of surface material, and the sorption properties of lindane onto cellulose acetate are not known. It is difficult to predict, therefore, the amount of sorption of lindane from the bulk fluid onto the reservoir surface, surface of pipe lines, and surface of the membrane filter itself, but it is known that invariably some sorption must occur. Many cases are described in literature of lindane adsorption by clays (16).

Another consideration in working with sparingly soluble substances is that even at the lower concentrations utilized, the lindane was practically at saturation value. The 17.2 and 34.4 μg/l solutions were 25 per cent and 50 per cent saturation utilizing an initially saturated solution. In order to obtain the 1,930 μg/l solution, it was necessary to dissolve the lindane in benzene, distill off the benzene and recrystalize the lindane. Freshly recrystalized lindane has greater solubility in water, and therefore it was possible to increase the lindane concentration to 1,930 μg/l by this recrystalizing process. In working with solutions which are at 25%, 50%, and 100% saturation there is some doubt as to whether the lindane present is in true solution or in some form of semi-colloidal dispersion. If the lindane were in true solution, as is assumed in this study, then all portions of a sample would be representative of that sample. If there were partial colloidal dispersion, however, then a sample may not be truly homogeneous, and a portion of a sample could possibly contain more or less of such colloidal groups than the total sample and therefore may not be representative. As discussed by Hindin (59) the form of organic matter under these circumstances is not entirely known.

Adsorption of lindane onto the cellulose acetate membrane and subsequently bleeding through the membrane, or retention of lindane within the structure of the membrane itself followed by subsequent bleeding into the permeate was exhibited when the same membrane was later utilized to test its rejection efficiency with the chemical pentachlorophenol. Gas chromatograph analysis of pentachlorophenol in the permeate following membrane separation indicated 62.4 μg/l lindane present in the permeate sample. On the basis of these results and based upon the membrane surface area of 46 cm^2 and a thickness of 0.01 cm, it is estimated that the membrane could have contained as much as 340 times the amount of lindane stored within it as was found in the final permeate sample of the lindane test.

5.5 PENTACHLOROPHENOL STUDIES

Early studies on pentachlorophenol were made utilizing the gas chromatograph for detection purposes, but it was found that the compound fouled the detector, or possibly the column, of the gas chromatograph. Since the chromatograph was a borrowed instrument, it was impossible to pursue further its use for pentachlorophenol studies.

Ultraviolet spectrophotometry at a wave length of 303 mμ was found to be the most suitable for measuring pentachlorophenol following its extraction from the aqueous phase by benzene. Spectrophotometric absorbance curves of various concentrations of pure compound pentachlorophenol in benzene are shown in Fig. 18. No interferences were observed, and the data followed Beers Law as shown by the calibration curve plotted in Fig. 13.

It was found that the benzene tended to dissolve portions of the teflon sealing compound utilized for joints in the reverse osmosis cell, reservoir, and piping system. This sealing compound exhibited an absorption interference peak at 285 mμ wave length. Figure 19 shows the UV absorption curves obtained on bulk fluid and permeate samples in two experiments, utilizing an initially saturated solution of pentachlorophenol for both studies.

It can be seen that although the broad interference band prohibited precise measurement of pentachlorophenol rejection by the membrane

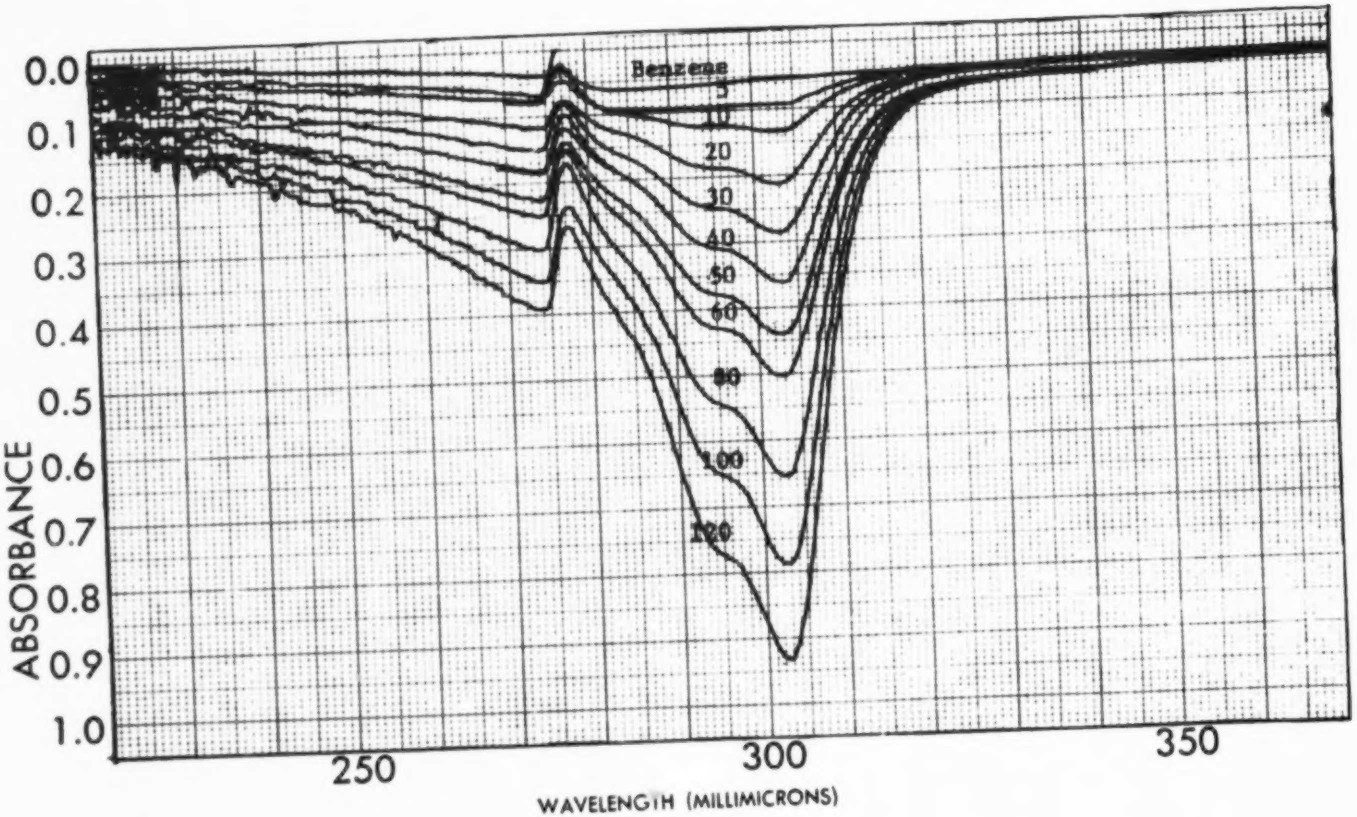

Fig. 18 UV SPECTROPHOTOMETER CURVES FOR KNOWN CONCENTRATIONS OF PENTACHLOROPHENOL

process, general observations can be made. In the first experiment, represented by the uppermost set of curves in Fig. 19, the 30 psi operation yielded a permeate enriched in the organic contaminant while the 50 psi operation yielded a solute rejection. The bulk fluid in the reservoir picked up increasing amounts of interfering contaminant as the study progressed, however, as shown by the considerable difference between the initial and final reservoir curves.

In the second series of studies, the interference in the reservoir changed dramatically as the test progressed. Under 30 psi conditions or operation there appeared to be slight permeate enrichment, while at 50 psi the interference made comparison with any reservoir curve impractical so that no conclusion was drawn. The 50 psi result is in substantial agreement with those reported by Hindin (59). On the other hand, the results at 30 psi agree with those obtained by Lonsdale (46) in studying the permeation of phenol through cellulose acetate membranes.

5.6 RELATED STUDIES ON LOW-MOLECULAR-WEIGHT ORGANIC COMPOUNDS

Lonsdale, et al (46) conducted research on the transport of phenol through cellulose acetate membranes. They found that phenol was transported much more rapidly than inorganic salts which they had previously studied. In phenol sorption experiments these researchers found that the diffusion coefficient for phenol in water-saturated 39.8 wt-% acetyl cellulose acetate was $9.6 \times 10^{-10} cm^2/sec$,

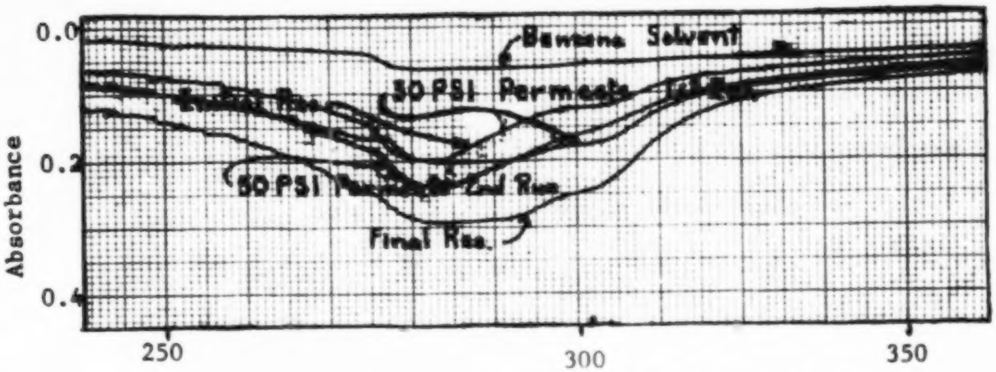

Fig. 19 PENTACHLOROPHENOL RESULTS (1st Run)

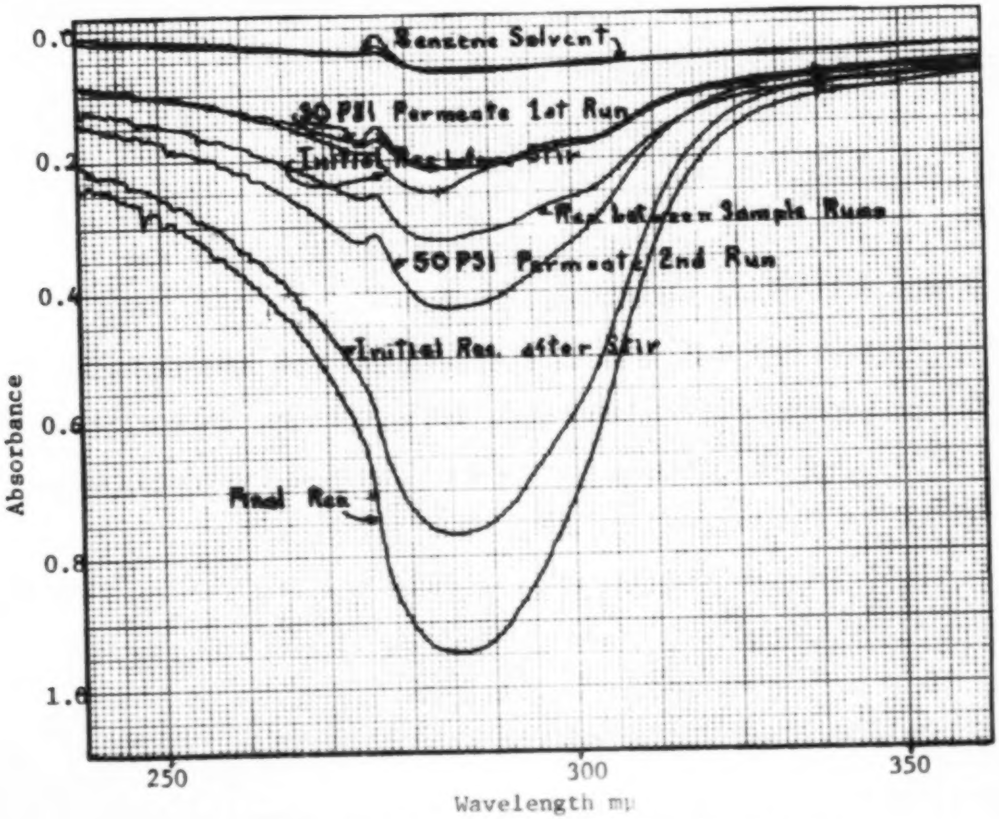

Fig. 19 PENTACHLOROPHENOL RESULTS (2nd Run)

and the equilibrium distribution coefficient between the acetate phase and water was 42. The diffusion coefficients for both sodium chloride and phenol were found to be almost identical. However, the distribution coefficients were very different; 42 for phenol and 0.03 for sodium chloride. This high sorption of phenol in the membrane was thought to be responsible for the high permeability of phenol through the membrane.

In the experimental results, permeate enrichments of more than 20% were reported. The study is significant because phenol and lindane molecules are similar in molecular size, shape, and weight. The results of the present studies indicated the possibility of high sorption of lindane by cellulose acetate.

Recently published data by Hindin, et al (59) has provided information relative to alkyl benzene sulphonate, lindane, chlorophenol and phenol. These tests were performed at a temperature of 25°C, a pressure of 100 atmospheres, and utilizing a Schleicher and Schuell Type B-18 cellulose acetate which had been immersed in water at 82°C for 30 minutes.

Table 10 shows the rejections obtained by Hindin for ABS, lindane, phenol and chlorophenol. In the lindane experiments performed by Hindin, the feed concentration was low, 500 ng/1 as compared to the present study's low of approximately 7,000 ng/1. The pressures utilized were also 1500 psi in Hindin's work as opposed to a high of 50 psi in the present study. In addition, the Abcor HFA-100 membrane is considerably more permeable than the membrane used in Hindin's study. It was projected that the Abcor membrane would have a flux of 105 gfd at 1500 psi based on a flux of 3.5 gfd at 50 psi and 25°C. The Schleicher and Schuell membrane had a flux of 16 gfd under the same conditions.

TABLE 10

REJECTION OF ORGANIC MOLECULES (59)

Chemical Species	Flux gal/ft²/day	Concentration Feed amt/l	 Product amt/l	Reduction %
ABS	16	1.06mg	0.06mg	94.0
	14	5.30mg	0.52mg	90.0
	18	10.60mg	1.94mg	82.0
Lindane	18	50.0 ng	8.0 ng	84.0
	16	500.0 ng	133.0 ng	73.4
Phenol+Chlorophenol	10.2			
Phenol		10.1 mg	8.3 mg	17.8
Chlorophenol		9.5 mg	3.2 mg	66.3
Phenol+Chlorophenol	11.6			
Phenol		101.0 mg	82.8 mg	18.0
Chlorophenol		106.0 mg	23.0 mg	78.3
Phenol+Chlorophenol	9.4			
Phenol		1031.0 mg	844.0 mg	18.1
Chlorophenol		1165.0 mg	267.0 mg	87.0

A good comparison can be made between the present results for ABS and Hindin's results. Although a tighter membrane and higher pressure were used by Hindin the ABS rejection's were reasonably comparable to the present results. At a pressure of 50 psi and concentration of .5 ppm ABS the rejection was 76% in the present study while for 1500 psi and a concentration of 1.06 ppm the rejection was 94% in Hindin's work.

The great differences in pressure and concentration seem to make a comparison of lindane results meaningless. Hindin achieved some rejection of lindane; however, the great differences in concentrations used may be significant, since solute flux increases with concentration. The present studies indicate low efficiency in lindane rejection. Either solute sorption by the membrane or possibly the precipitation of lindane on the membrane surface, due to a combination of low lindane solubility and concentration polarization, seem to have occurred in the present study. This conclusion was drawn from the time dependency of the solute permeation.

6. CONCLUSIONS

On the basis of studies conducted on reverse osmosis treatment of water containing organic contaminants, the following conclusions may be drawn:

1. Observed water flux rates increased with increasing temperatures in the temperature range of 24 to 35°C.
2. The membranes utilized in this study, which were developed primarily for operation at high pressures, were found to produce satisfactory rejection of ABS at low pressures of 30 to 50 psi.
3. Rejection of ABS varied from 76 to 41 per cent in the concentration range of 0.5 to 4 ppm.
4. Preliminary lindane results indicate rejection efficiency to be quite low in the concentration range of .00739 to 1.93 mg/l at 30 to 50 psi.
5. Lindane enrichment of the membrane or precipitation on the surface of the membrane appeared to occur with the passage of time.
6. Preliminary pentachlorophenol results indicate solute rejection at 50 psi and permeate enrichment at 30 psi.
7. Laboratory results with the Abcor HFA-100 membrane indicate good removal of ABS but indicate the need for a tighter membrane and/or higher pressures for lindane and pentachlorophenol removal.

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APPENDIX I

OPERATING PARAMETERS FOR ELECTRON CAPTURE GAS CHROMATOGRAPH

Aerograph Model 600-C

(Wilkens Instrument and Research, Inc.)

Column	Pyrex 5 ft. long x 1/8 in. inside diameter
Packing	5% Dow-11 on Chromosorb "W" 60/80 mesh
Temperatures	195°C oven 195°C detector 220°C injector block
Gas	Nitrogen pre-purified
Gas Flow	50-60 ml/min.
Voltage	90 volts applied to anode
Standing Current	2 x 10^{-8} amps
Attenuation	2, 4, 8
Range	1, 10

APPENDIX II

SAMPLE REGRESSION ANALYSIS OF DATA ON WATER FLUX, TEMPERATURE, AND PRESSURE RELATIONSHIPS

Data page 72   50 psi

$$y = \bar{y} + b(x-\bar{x})$$

x = temperature
y = water flux gal/ft^2/day
N = number of points
b = slope of regression line

x	y	xy	x^2
24.0	3.46	83.0	576.0
28.5	3.79	108.0	812.2
29.0	3.86	111.9	841.0
31.5	3.90	122.8	992.2
32.0	4.02	128.6	1,024.0
32.5	4.06	132.0	1,056.2
35.0	4.31	150.8	1,225.0

$\Sigma x = 212.5$ $\Sigma y = 27.40$ $\Sigma xy = 837.3$ $\Sigma x^2 = 6{,}526.8$

$$\bar{x} = \frac{\Sigma x}{N} \qquad \bar{y} = \frac{\Sigma y}{N}$$

$$\bar{x} = \frac{212.5}{7} \qquad \bar{y} = \frac{27.4}{7}$$

$$\bar{x} = 30.36 \qquad \bar{y} = 3.91$$

$$b = \frac{\Sigma xy - \dfrac{(\Sigma x)\ (\Sigma y)}{N}}{\Sigma x^2 - \dfrac{(\Sigma x)^2}{N}}$$

$$b = \frac{837.3 - \frac{(212.5)\ (27.4)}{7}}{6526.8 - \frac{451\text{[illegible]}}{7}} = .071$$

$$y = 3.91 + .071\ (x - 30.36)$$

APPENDIX III

REGRESSION ANALYSIS DATA ON WATER FLUX, TEMPERATURE, AND PRESSURE RELATIONSHIPS

Fig. 14, Page 73

50 psi	$y = 3.91 + .071\ (x-30.36)$
40 psi	$y = 3.38 + .073\ (x-33.31)$
30 psi	$y = 2.47 + .0302\ (x-31.35)$

Fig. 15, Page 76

50 psi	$y = 3.51 + .067\ (x-30.38)$
40 psi	$y = 2.93 + .09\ (x-31.66)$
30 psi	$y = 2.13 + .028\ (x-29.88)$